Study on manipulating photonic environment of emitters with scale dependent optical cavities

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Study on Manipulating Photonic Environment of Emitters with Scale Dependent Optical Cavities

HOU SONGYAN

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

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Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 3 is published as Hou S, Xie A, Xie Z, Tobing LY, Zhou J, Tjahjana L, Yu J, Hettiarachchi C, Zhang D, Dang C, Birowosuto MD, Edwin HTT, Wang H. “Concurrent inhibition and redistribution of spontaneous emission from all inorganic perovskite photonic crystals” *ACS Photonics* **2018**.

The contributions of the co-authors are as follows: Xie A prepared the perovskite samples and Hou S, Zhou J and Tjahjana L fabricated photonic crystals using the EBL and RIE. Xie Z did the FDTD simulation, and Hou S, Birowosuto MD, Tobing LY, Yu J and Hettiarachchi C conducted optical characterizations under the supervision of Zhang D, Dang C, Edwin HTT, Wang H.

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The contributions of the co-authors are as follows: Hou S, Wang X and Zhou J prepared the 2D materials and fabricated the devices under the supervision of BKT and Teo EH. Hou S, Birowosuto MD, Tobing LY and Yu J performed the optical measurement under the guidance of Zhang D, Dang C, Coquet P and Wang H. Hou S, Tobing LY, Xie Z and Birowosuto MD developed the comprehensive analytical and theoretical simulations. Edwin HTT and Wang H supervised the whole project. All authors discussed the results and wrote the article.

Chapter 5 is published as Hou S, Birowosuto MD, Umar S, Anicet MA, Tay RY, Coquet P, Tay BK, Wang H, Teo EH. “Localized emission from laser-irradiated defects in 2D hexagonal boron nitride” *2D Materials* **2017**.

The contributions of the co-authors are as follows: Hou S, Umar S, Anicet MA prepared the sample and conducted the laser ablation experiment under the supervision of Tay RY, Coquet P, Birowosuto MD, Tay BK, Wang H, Teo EH. Hou S conducted all the optical measurement and prepared the manuscript. All authors discussed the results and wrote the article.

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Summary

Photon emitters placed into an optical cavity will experience a surrounding photonic environment change, which is essential to push nanophotonic devices into the practical realm, including photonic switches, quantum networking and nano-lasers. Spontaneous emission of emitters plays a critical role in determining the performance of many photonic devices. Both dielectric microcavity and plasmonic nanocavity provide a platform to control the decay channels of integrated emitters, and their coupling strength, g , yields: $g \propto \sqrt{N/V}$, where N is the involved number of excitons and V is the mode volume of a cavity. The coupling strength can be enhanced by scaling down the cavity volume. Although it difficult to boost this interaction in individual single photon emitters, approaching the quantum limit of coherent interactions between individual quantum emitters and cavity resonators is crucial for fundamental quantum mechanics as well as practical applications.

In this thesis, we investigated the light-matter interaction by coupling emitters with photonic and plasmonic optical cavities. We scaled down both cavity volume from photonic crystals to gap plasmonic nanocavities and the size of emitters from film, monolayer to localized single photon sources. Photonic emitters experienced a photonic environment change from broadband confinement in photonic crystals to extreme field confinement in gap plasmonic nanocavities. By scaling down the size of the cavity volume from micrometers to nanometers, we successfully manipulate light emission with high extraction in photonic crystals at weak coupling regime and strong light-matter interaction in plasmonic nanocavities. Finally, we also demonstrated single photon emitters in laser irradiated hexagonal boron nitride monolayers and the modification of spontaneous emission of quantum emitters using plasmonic resonators.

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Chapter 1 Introduction

The possibility to control the interaction between light and matter has initiated substantial interest in building nanostructure-based hybrid photonic systems with novel functionalities. Although human has been trying to control light using mirrors and lens since long time ago, the nature of light only has started to be unveiled during the past decades. Of major improvement is the development of quantum mechanics to describe the interaction between light and matter, raised by James C. Maxwell and culminated with the quantum electro-dynamics (QED) theory. While the well-established quantum theory of light successfully describes the nature of light-matter interaction, manipulating light-matter interaction in quantum systems is still a big challenge owing to the sub-wavelength scale requirement. Benefiting from the exciting improvements in nanoscale fabrication techniques like electron beam lithography (EBL) and reactive ion etching (RIE), we can finally fabricate complex nanostructures with ultra-small feature size, realizing the manipulation over light at nanoscale. This paves the way toward the new applications of light-matter interaction using nanostructures[1].

1.1 Theory of Light-Matter Interaction

In well-known two-level system, a charged atom has two essential energy levels and negligible coulomb interactions at low temperature, and the two states are defined as ground state $|g\rangle$ and excited state $|e\rangle$. The transitions between the two states can be described as two operators:

$$\begin{aligned}\sigma &= |g\rangle\langle e| \\ \sigma^\dagger &= |e\rangle\langle g|\end{aligned}\tag{1.1}$$

The dipole moment of an atom $\vec{d}$ is determined by its position:

$$\vec{d} = -e_0 \vec{x} \quad (1.2)$$

Then the dipole moment operator can be decomposed as:

$$\begin{aligned} \hat{d} &= |g\rangle \vec{d}_{ge} \langle e| + |e\rangle \vec{d}_{ge}^* \langle g| \\ \vec{d}_{ge} &= \langle g | \vec{d} | e \rangle \end{aligned} \quad (1.3)$$

Now we can write the total Hamiltonian of the atom interacting with light field $\vec{E}(t)$:

$$H = \hbar \omega_e \sigma^\dagger \sigma + \hbar \omega_g (1 - \sigma^\dagger \sigma) - (\sigma \vec{d}_{eg} \vec{E}(t) + \sigma^\dagger \vec{d}_{eg}^* \vec{E}(t)) \quad (1.4)$$

In some cases, the transition of dipole moment can be real and therefore, we set $\vec{d} = \vec{d}_{ge} = \vec{d}_{ge}^*$. We

can now write the final Hamiltonian of a two-level system:

$$H = \hbar \omega_g + \hbar(\omega_e - \omega_g) \sigma^\dagger \sigma - \vec{d} \cdot \vec{E}(t) (\sigma^\dagger + \sigma) \quad (1.5)$$

and the interacting energy between the dipole and electric field is:

$$H_{\text{int}} = -\vec{d} \cdot \vec{E}(t) (\sigma^\dagger + \sigma) \quad (1.6)$$

By engineering the photonic environment surrounding the emitter using an optical cavity, we can explore fascinating light-matter interaction phenomena, such as weak coupling with modified spontaneous emission known as Purcell factor and strong coupling with hybridized eigenstates. The emitter-cavity coupling is determined by three parameters: coupling strength, g , damping rate of the cavity, Γ_{cav} , and the intrinsic spontaneous emission rate of exciton, Γ_{exc} . The system is in weak coupling regime if $g \ll (\Gamma_{\text{exc}}, \Gamma_{\text{cav}})$ and reaches strong coupling regime when $g \gg$

$(\Gamma_{exc}, \Gamma_{cav})$. Hybridized states in strong coupling regime occurs when the coherent energy exchange is faster than dissipation channels.

The interaction between photonic emitters and optical cavities opens up many possibilities for the applications in nanophotonics. Spontaneous emission in emitters is a fundamental factor limiting the performance of photonic devices, such as quantum information processing[2], nano-lasers[3], solar cells[4] and LEDs[5]. In weak coupling regime, the modified spontaneous emission enables plenty of photonic device applications, from low-threshold lasers to bright quantum emitters. For quantum light sources including molecules and semiconductors quantum dots, their spontaneous emission rate is in the order of 100-1000 MHz, limited by both the low localized density of photonic states and the small emitters size. These slow emission rates greatly prohibit the high-speed operation of photonic devices. Improved photonic environment of emitters has been achieved by a few approaches including dielectric cavities and plasmonic nanocavities. The photonic density of states of emitters is largely increased when coupled with optical cavities in weak coupling regime. The radiative lifetimes are strongly modified with faster emission rates, providing a bridge between ultrafast emitters and highspeed photonic devices. In strong coupling regime with mixed hybridized states, the new polariton states with both light and matter characters are of great importance for multiple novel photonic applications like polariton switches[6], polariton lasers[7, 8] and quantum computing[9, 10]. Approaching quantum limit of strong light-matter interaction between single photon sources and resonant cavities enables a host of potential applications in quantum optics, such as quantum communications[10] and quantum networks[11].

1.1.1 Weak Coupling

In weak coupling regime, the coupling or energy exchange rate is slower than other intrinsic dissipation rates:

$$g < \frac{1}{2}(\Gamma_{exc} + \Gamma_{cav}) \quad (1.7)$$

where g is the coupling strength between exciton and plasmon (photon), Γ_{exc} and Γ_{cav} denote the dissipation rates of exciton and plasmon (photon). In this regime, the energy exchange rate largely depends on the density of initial and final states according to Fermi's Golden Rule:

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f | H | i \rangle \right|^2 \rho(E_f) \quad (1.8)$$

where $\Gamma_{i \rightarrow f}$ is the energy exchange rate between initial and final states, $\rho(E_f)$ is the density of final states. The states of a particle in a box size of V can be calculated through wavevector k :

$$\rho(k)dk = \frac{V}{2\pi^2} k^2 dk \quad (1.9)$$

For electromagnetic radiation in an optical cavity, the cavity photon energy dispersion relation is:

$$E = \frac{\hbar c}{n_{cav}} k \quad (1.10)$$

where $k^2 = k_{\perp}^2 + k_{\parallel}^2$, n_{cav} is the refractive index of cavity, and c is the speed of light. Then we can obtain the number of states whose energy is between E and $E+dE$ by changing the variables in equation (1.9) from wavevector k to energy E :

$$\frac{V}{2\pi^2} \frac{E^2 n_{cav}^3}{(\hbar c)^3} dE \quad (1.11)$$

Consider the number of modes q , we see that the density of states is given by:

$$\rho(E) = q \frac{V}{2\pi^2} \frac{E^2 n_{cav}^3}{(\hbar c)^3} \quad (1.12)$$

According to Fermi's Golden Rule, the spontaneous emission rate is determined by the density of states in hybrid system. The enhancement of spontaneous emission rate resulting from the change of electromagnetic density of states can be described by Purcell factor[12]:

$$F_p = \frac{3}{4\pi^2} \left(\frac{\lambda}{n} \right)^3 \left(\frac{Q}{V} \right) \quad (1.13)$$

in which λ is the wavelength in vacuum, n is the refractive index and Q is the quality factor of the cavity. Thus, the quality factor of cavity is the relevant figure of merit for achieving a large Purcell factor, since the enhancement also depends on the mode volume.

The effective mode volume V for the resonant mode in an optical cavity is defined by[13]:

$$V = \frac{\int \text{Re} \left(\frac{d(\omega \varepsilon(\vec{r}))}{d\omega} \right) |\vec{E}(\vec{r})|^2 d\vec{r}}{\max(\text{Re} \left(\frac{d(\omega \varepsilon(\vec{r}))}{d\omega} \right) |\vec{E}(\vec{r})|^2)} \quad (1.14)$$

The equation can be simplified by expanding the derivative:

$$V = \frac{\int \text{Re} \left(\omega \frac{d(\varepsilon(\vec{r}))}{d\omega} + \varepsilon(\vec{r}) \right) |\vec{E}(\vec{r})|^2 d\vec{r}}{\max(\text{Re} \left(\omega \frac{d(\varepsilon(\vec{r}))}{d\omega} + \varepsilon(\vec{r}) \right) |\vec{E}(\vec{r})|^2)} \quad (1.15)$$

The definition of the effective mode volume can be conceptualized in terms of integrating the electric fields over the volume of cavities, and normalized to the maximum electric field.

Quality factor Q of an optical resonator describes how undamped the resonator is. Quality factor of an optical cavity is generally defined in terms of the ratio of the energy stored to the energy loss in the cavity per cycle[3]:

$$Q = 2\pi \frac{\text{energy stored}}{\text{energy loss per cycle}} \quad (1.16)$$

And experimentally, Q can be calculated in terms of the cavity resonant frequency ω_{cav} and its full width at half maximum $\Delta\omega$ as:

$$Q = \frac{\omega_{\text{cav}}}{\Delta\omega} \quad (1.17)$$

Plasmonic based cavities usually have poor Q compared with photonic crystal cavities due to the light energy loss by the absorption in metals.

1.1.2 Strong Coupling

Fig. 1.1 Strong exciton-photon (plasmon) coupling in a two-level system. (a) Polariton in-plane dispersions at resonance. The black lines show the dispersion of photon (plasmon) and exciton while the orange lines demonstrate the dispersion of hybrid polaritons. (b) corresponding Hopfield coefficients. (c) Energy diagram of a coupled exciton-cavity hybrid polariton system. Figure from REF[14], © The Royal Society of Chemistry 2019.

If the coherent energy exchange between cavity and exciton is fast enough:

$$g > \frac{1}{2}(\Gamma_{exc} + \Gamma_{cav}) \quad (1.18)$$

Considering a system consisting of a two-level atom coupled into a single mode cavity in QED, the hybrid system can be described using well-known Jaynes-Cummings model[15] with new

eigenstates and quasiparticles. Then Hamiltonian of the system can be described by the sum of exciton, cavity and the interaction between exciton and plasmon (photon):

$$\begin{aligned}\hat{H}_{JC} &= \hat{H}_{exc} + \hat{H}_{cav} + \hat{H}_{int} \\ &= \frac{1}{2}\hbar\omega\hat{\sigma}_z + \hbar\omega_{cav}\left(\hat{a}'\hat{a} + \frac{1}{2}\right) + \hbar g_0(\hat{a}'\hat{\sigma} + \hat{a}\hat{\sigma}')$$

Where $\hat{\sigma}_z$, $\hat{\sigma}$ and $\hat{\sigma}'$ represent inversed, raising and lowering Pauli matrices, respectively, $\hat{a}$ and $\hat{a}'$ are electromagnetic mode operators for creation and annihilation. The $\hat{a}'\hat{\sigma}$ is related to the electronic transition from the ground to excited state with a photon simultaneously annihilated. When N excitons interact with the cavity, this model is then revised by replacing each $(\hat{\sigma}_z, \hat{\sigma}, \hat{\sigma}')$ with bosonic operator $\hat{b}$, and then the Hamiltonian can be expressed as:

$$\hat{H} \simeq \hbar\omega\left(-\frac{N}{2} + \hat{b}'\hat{b}\right) + \hbar\omega_{cav}\hat{a}'\hat{a} + \hbar g(\hat{a}'\hat{b} + \hat{a}\hat{b}')\tag{1.20}$$

where N is the number of excitons, g is the coupling strength: $g = g_0\sqrt{N}$.

Two coupled harmonic oscillators are employed to offer a physical analyzer for Jaynes-Cummings Hamiltonian. The interaction results in two new eigenstates with a mixture of light and matter characteristics, so called polaritons. Apart from the upper and lower polaritons, there are also dark nonradiative modes which are not observable using traditional optical techniques[16]. The two split polaritons states are given by:

$$\begin{aligned}|P, +\rangle &= \alpha|e, 0\rangle + \beta|g, 1\rangle \\ |P, -\rangle &= \beta|e, 0\rangle - \alpha|g, 1\rangle\end{aligned}\tag{1.21}$$

The contributions of exciton and plasmon (photon) to polaritonic states can be extracted with $|\alpha|$ and $|\beta|$, termed as Hopfield coefficients[17]:

$$\begin{aligned}
|\alpha|^2 &= \frac{1}{2} \left(1 + \frac{E_{exc} - E_{cav}}{\sqrt{(E_{exc} - E_{cav})^2 + 4g^2}} \right) \\
|\beta|^2 &= \frac{1}{2} \left(1 - \frac{E_{exc} - E_{cav}}{\sqrt{(E_{exc} - E_{cav})^2 + 4g^2}} \right)
\end{aligned} \tag{1.22}$$

At resonance with zero detuning, the two polariton states are exactly half light and half matter with $|\alpha|^2 = |\beta|^2 = \frac{1}{2}$ (Fig. 1.1b). The energy separation between the two polaritons is called Rabi splitting $\hbar\Omega$ (Fig. 1.1c), which can be expressed as [18, 19]:

$$\begin{aligned}
\hbar\Omega &= 2\hbar g \\
&= 2d\sqrt{N}\sqrt{\hbar\omega_{cav}/2\varepsilon_0V}
\end{aligned} \tag{1.23}$$

For an in-plane optical cavity, the energy can be expressed as:

$$E_{cav} = \frac{\hbar c}{n_e} \sqrt{\left(\frac{m\pi}{T_{cav}}\right)^2 + k_{\parallel}^2} \tag{1.24}$$

where c is the speed of light in the vacuum, n_e represents the refractive index of the environment, m is the number of cavity modes and T_{cav} is the thickness of the cavity. $k_{\parallel}$ is the in-plane wavevector and is determined by the wavelength λ and the angle of incidence θ :

$$k_{\parallel} = \frac{2\pi}{\lambda} \sin \theta \tag{1.25}$$

The energy of cavity shows a strong in-plane dispersion while that of exciton is independent of $k_{\parallel}$, as the energy of exciton is determined by the bandgap of materials and demonstrates no dispersion with respect to the incidence wavevector, as shown in Fig.1.1a. Inherited from photonic

environment induced by the cavity, the polaritonic states will demonstrate an in-plane dispersion behavior when coupled to an in-plane mode cavity as shown in Fig. 1.1a.

The hybrid polariton states with both light and matter characters is of great importance for multiple novel photonic applications like polariton switches[6], polariton lasers[7, 8] and quantum computing[9, 10].

1.2 Optical Microcavities

	Fabry-Perot	Whispering gallery	Photonic crystal
High Q	<p>Q: 2,000 V: 5 (λ/n)³</p>	<p>Q: 12,000 V: 6 (λ/n)³</p> <p>Q_{III-V}: 7,000 Q_{Poly}: 1.3×10^5</p>	<p>Q: 13,000 V: 1.2 (λ/n)³</p>
Ultrahigh Q	<p>F: 4.8×10^5 V: 1,690 μm^3</p>	<p>Q: 8×10^9 V: 3,000 μm^3</p> <p>Q: 10^8</p>	

Fig. 1.2 Overview of the optical confinement performances in optical microcavities. The characteristics are taken from the following cited references. Upper row: micropillar[20], microdisk[21], semiconductor[22], polymer add/drop[23] filter and photonic crystal[24]. Lower row: Fabry-Perot bulk optical cavity[25], microsphere[26] and microtoroid[27]. Adapted from REF[28], © 2003 Nature Publishing Group.

Optical microcavities possess the capability to confine light into small volumes within diffraction limit. Optical microcavities based devices have attracted wide attention due to their great potential in various optoelectronic applications. For example, laser emission can be modified into narrow

spot size in optical microcavities made from III-V semiconductors. In quantum devices, atoms or quantum dots coupled with optical microcavities can emit photons in a desired direction and these microcavities also provide a photonic environment to achieve quantum interaction between spontaneous radiation and matter. Quality factor and mode volume are prominent characteristics in optical microcavities, and an overview of these typical values is given in Fig. 1.2. Besides, there are two representative methods of confinement employed in optical microcavities: dielectric resonators and photonic crystals cavities.

1.2.1 Dielectric Resonators

Dielectric resonators with high index and simple shapes have demonstrated size dependent resonance with advanced electromagnetic functions[29, 30]. Micropost Fabry-Perot cavity and whispering gallery resonator are the most widely used dielectric resonators. Micropost cavities offer platforms for coupling and manipulating emitted photons from quantum dots. The Bragg mirrors at two sides of emitters give rise to one-dimension mode confinement, as shown in Fig. 1.2. And whispering gallery microcavities can be found in several geometries including spheres, disks and rings. Directional scattering has been demonstrated in semiconductor nanoparticles which can satisfy the renowned Kerker conditions. This directionality results from the coherent resonances of electric excitation and magnetic dipole, and can be achieved even at visible wavelength due to their high index. The unique directionality in dielectric resonators makes it possible to control over the direction and polarization of the emission field without additional components like back reflectors, which opens great possibility in optoelectronic applications.

1.2.2 Photonic Crystals

Fig. 1.3 Schematic of Bragg diffraction. Two identical incident light are scattered off from consecutive lattice atoms. Constructive interference occurs when the optical path difference is integer multiple of the wavelength.

Photonic crystals are (PhCs) artificially made from periodic dielectric materials. They provide a promising platform for passively guiding the light flow and produce unprecedented quantum effects. Such a periodic structure generates a photonic bandgap to prohibit the propagation of light in any direction inside the layer due to the Bragg diffraction. Bragg diffraction is well known to occur when the light wavelength is comparable to the distance of crystal lattice planes (Fig. 1.3).

The Bragg condition is described as:

$$m\lambda = 2d \sin \theta \quad (1.26)$$

where m is a positive integer, d is the spacing between lattice planes. This Bragg diffraction results in the forbidden range of frequency with so-called stop band and the photonic band gap is the grouped region of stop band. The reflection peak with constructive interference occurs when path length is a multiple of the radiation wavelength. Since the PhCs device was firstly proposed to build a photonic insulator by Yablonovitch in 1987, PhCs devices have emerged as promising and unique platforms for photonic devices with a great potential in the applications in optical switches,

lasers, optical waveguides and quantum computing system. Of the major interest is its comparability to chip-scale photonic circuits integration, which can largely improve the performance of lasers[31], modulators[32] and waveguides[33], as shown in Fig. 1.4.

Fig. 1.4 Schematic illustrations of photonic circuits with PhCs integrated. (a) Schematic of a 2D semiconductor nanolaser, with WSe₂ monolayer on top of PhCs. (b) Schematic of the graphene electro-optic modulator integrated with PhCs. (c) Schematic of alligator PhCs waveguide to reach superradiance. Panel (a) is adapted from REF[31], © 2015 Macmillan Publishers Limited. Panel (b) is adapted from REF[32], © 2015 American Chemical Society. Panel (c) is adapted from REF[33], © 2015 American Physical Society.

$$\begin{aligned}
 \nabla \cdot \bar{\bar{D}} &= \rho \\
 \nabla \cdot \bar{\bar{B}} &= 0 \\
 \nabla \times \bar{\bar{E}} &= -\frac{\partial \bar{\bar{B}}}{\partial t} \\
 \nabla \times \bar{\bar{H}} &= \bar{\bar{J}} + \frac{\partial \bar{\bar{D}}}{\partial t}
 \end{aligned} \tag{1.27}$$

The electromagnetic field in PhCs is governed by the four Maxwell's equations, where $\vec{E}$ and $\vec{H}$

are electric and magnetic fields, $\vec{D}$ and $\vec{B}$ are constitutive relations. ρ and $\vec{J}$ are the free charge and current density, respectively. For an isotropic dielectric material interacting with a weak electromagnetic field and its response in a linear regime, $\vec{D}$ is dependent on the electric field $\vec{E}$:

$$\vec{D}(r, \omega) = \varepsilon(r, \omega) \vec{E}(r, \omega) \quad (1.28)$$

The dielectric constant $\varepsilon(r, \omega)$ can be treated as real and positive values in losses transparent materials, and the dependence of frequency on $\varepsilon(r, \omega)$ can be negligible: $\vec{D}(r) = \varepsilon(r) \vec{E}(r)$. We focus primarily on dielectric materials with the unitive magnetic permeability, we can get $\vec{B}(r) = \mu_0 \vec{H}(r) = \vec{H}(r)$. Given the assumptions mentioned above, we can rewrite down Maxwell's equations in (1.27) as:

$$\begin{aligned} \nabla \cdot \varepsilon(r, \omega) \vec{E}(r, t) &= 0 \\ \nabla \cdot \vec{H}(r, t) &= 0 \\ \nabla \times \vec{E}(r, t) &= -\mu_0 \frac{\partial \vec{H}(r, t)}{\partial t} \\ \nabla \times \vec{H}(r, t) &= \varepsilon(r) \frac{\partial \vec{E}(r, t)}{\partial t} \end{aligned} \quad (1.29)$$

Even though both $\vec{E}$ and $\vec{H}$ are complicated functions of space and time, we still can use harmonic modes to separate the time and space dependence. We first expand the fields into complex exponentials:

$$\begin{aligned} \vec{H}(r, t) &= \vec{H}(r) e^{-i\omega t} \\ \vec{E}(r, t) &= \vec{E}(r) e^{-i\omega t} \end{aligned} \quad (1.30)$$

We insert these two equations into Maxwell's equations (1.29) and can get the conditions:

$$\begin{aligned}\nabla \cdot \vec{H}(r) &= 0 \\ \nabla \cdot [\varepsilon(r)\vec{E}(r)] &= 0\end{aligned}\tag{1.31}$$

which gives a physical conclusion that there is no light source or annihilation of displacement and magnetic fields. We now focus on the other two Maxwell's curl equation:

$$\begin{aligned}\nabla \times \vec{E}(r) - i\omega\mu_0\vec{H}(r) &= 0 \\ \nabla \times \vec{H}(r) + i\omega\varepsilon(r)\vec{E}(r) &= 0\end{aligned}\tag{1.32}$$

Given that the dielectric and magnetic permeability constants can be combined with $c = 1/\sqrt{\varepsilon_0\mu_0}$, then we can get the equation from (1.32) entirely in $\vec{H}(r)$:

$$\nabla \times \left(\frac{1}{\varepsilon(r)} \nabla \times \vec{H}(r) \right) = \left(\frac{\omega}{c} \right)^2 \vec{H}(r)\tag{1.33}$$

Together with equation (1.31), we can obtain explicit details about $\vec{H}(r)$. Then we can use equation (1.32) to extract $\vec{E}(r)$:

$$\vec{E}(r) = \frac{i}{\omega\varepsilon(r)} \nabla \times \vec{H}(r)\tag{1.34}$$

Fig. 1.5 Simple illustrations of PhCs with periodicity in one, two and three dimensions. Figure from REF[34], © 2008 Princeton University Press.

To reveal the electromagnetic field dispersion in PhCs, the photonic band structures are proposed to describe the dispersion relations of electromagnetic waves. PhCs can be formed in one, two and three dimensions according to their periodicity (Fig. 1.5). Here we use one-dimensional (1D) PhCs as an example to simplify the complexity. The 1D PhCs are constructed by alternating two dielectric thin layers with periodic refractive indices, (n_1 and n_2), in z direction, as shown in Fig. 1.6. Now we induce Bloch states into equation (1.33) with information given by the materials index n , wave vectors in z direction k_z and in-plane k_{xy} :

$$\bar{H}_{n,k_z,k_{xy}} = e^{((ik_z \cdot z) + (ik_{xy} \cdot \rho))} \mu_{n,k_z,k_{xy}}(z) \quad (1.35)$$

Here $\mu_{n,k_z,k_{xy}}(z)$ has a periodicity of lattice constant R in z direction: $\mu_{n,k_z,k_{xy}}(z) = \mu_{n,k_z,k_{xy}}(z + mR)$.

Then we can obtain the dispersion relation by combining equation (1.35) with equation (1.34). The frequency at each band varies continuously because the wave vector k is a continuous parameter. In this way, we are finally at the description of electromagnetic fields in PhCs: they are a group of continuous functions of frequencies over the wave vector.

Fig. 1.6 The PhCs with 1D periodicity.

The enhanced interaction between light and matter can be evaluated by the Purcell factor. The spontaneous emission rate enhancement is proportional to Q/V at resonance. Therefore, we can increase the cavity effect on an emitter at resonance by increasing the Q or decreasing the mode volume. The case in practice is that V is usually largely limited by the diffraction in dielectric materials. The ultimate mode of volume in a cavity is determined: $V \approx 2(\lambda/2n)^3$ [35], which leads to the emerging interest in plasmonic nanocavities.

Optical microcavities exhibit extremely high quality factor, thus, they form promising basis of low-threshold nano-lasers or promote light-matter interaction into strong coupling regime. However, these systems suffer from the badly confined optical modes which are diffraction limited. Therefore, improved confinement of optical modes is then developed using plasmonic nanocavities to promote light-matter interaction at nanoscale.

1.3 Plasmonic Cavities

Progress towards high performance dielectric cavities discussed above has been hindered by the diffraction limit of electromagnetic fields, which results in the difficulty of reducing the mode volume much smaller than the optical wavelength of interest ($V_\lambda = (\lambda/n)^3$). Improved

confinement of optical fields has been realized using plasmonic cavities with ultra-small mode volume. With careful design and precise fabrication, the mode volume V of a plasmonic nanocavity can be reduced to $V_\lambda \times 10^{-6}$ with a few hundreds of quality factor. These unique properties of plasmonic nanocavities open up a new level control over light beyond the diffraction limit.

1.3.1 Surface Plasmons

Surface plasmons (SPs) are light waves which propagate along the metallic surface due to their strong interaction with collective oscillation of free electrons the metal surface (Fig. 1.7a). SPs have been widely reported since the pioneering work by R. H. Ritchie in 1957[36]. This resonant interaction between electromagnetic modes of light and surface electrons is tightly bound to the interface between the metal and dielectric medium, and the modes can be confined into a volume below diffraction limit if the conductor is well shaped. Concentrating light flow with SPs results in enhanced electromagnetic field to engineer photonic environment and boot fascinating physical phenomena. This appealing feature also opens the possibility to carry electrical signal using SPs by embedding them into photonic circuits at subwavelength scale.

Before quantitatively understand the properties of SPs, we first analyze the optical properties of metal first. The dielectric constant of metals can be dictated with Drude's model[37]:

$$\begin{aligned}\varepsilon_{metal}(\omega) &= 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau_e)} \\ \omega_p^2 &= \frac{ne^2}{m_e}\end{aligned}\tag{1.36}$$

Here ω_p is electron plasma frequency which determines the highest response frequency of electrons in the metal, $1/\tau_e$ is the damping rate of electrons which is a determinative parameter of

metal loss. Table 1.1 shows the plasma frequency and damping rate of some typical metals in the infrared and far infrared. The equation (1.36) also draws a conclusion that if $\omega < \omega_p$, the dielectric constant is negative and the light waves cannot propagate in the metal. The SPs dispersion relation can be determined by solving Maxwell's equations with a frequency dependent SP wavevector, k_{SP} :

$$k_{SP} = k_0 \sqrt{\frac{\epsilon_d \epsilon_{metal}}{\epsilon_d + \epsilon_{metal}}} \quad (1.37)$$

If the SPs are generated at metal-dielectric interface, the permittivity of metal, ϵ_{metal} , should have opposite signs to that of dielectric medium, ϵ_d . The driven field in perpendicular direction is enhanced near the interface and decays exponentially into the bulk(Fig. 1.7b). The non-radiative nature of SPs leads to the field in perpendicular direction being evanescent and confines the light energy on the metal-dielectric interface. The decay length of the field in dielectric medium, δ_d , is of the order of half resonant wavelength while that in metal, δ_m is dependent on the skin depth which is a determinative parameter on feature size in SPs-based photonic circuits. The dispersion relation of SPs in Fig. 1.7c shows that SPs mode has a larger wavevector than that of free space photon at the same frequency and this mismatch of the wavevector must be bridged to evoke the generation of SPs.

Fig. 1.7 SPs properties. (a) SPs polariton on metal-dielectric interface with transverse magnetic character. (b) The electric field intensity decaying exponentially with distance away from the interface. (c) The dispersion curve of SPs with mismatched momentum. Adapted from REF[38], © 2003 Nature Publishing Group.

Table 1.1: Optical properties of some typical metals from Drude model in the infrared and far infrared range. Adapted from REF[39], © 1985 Optical Society of America.

Metals	Silver	Aluminum	Gold	Copper	Platinum
Plasma frequency (PHz)	2.18	3.57	2.18	1.911	1.24
Damping rate (THz)	4.35	19.79	6.46	8.34	16.73

1.3.2 Emitter Dynamics near a Metal Surface

In this section, we will discuss the mechanism of an emitter close to a metallic mirror as shown in Fig. 1.8. All wave components are considered to offer deep insights on electrodynamics description of the emitter close to reflective metal surface. R.R. Chance, A. Prock and R. Silbey firstly derived this method in 1978[40], and then G.W. Ford and W.H. Weber extended it to various metallic surface in 1984[41].

Fig. 1.8 Schematic illustration of the wave components in dielectric-metal interface.

Considering a situation that a dipole near a metal surface (Fig. 1.8), this dipole moment, μ , is described as:

$$\mu = \mu_0 e \left[-i(\omega + \Delta\omega)t \right] e \left(-\frac{bt}{2} \right) \quad (1.38)$$

here $b = 1/\tau$ is the decay rate of dipole. $\Delta\omega$ is related to the frequency shift. The reflective electric field intensity can be described by:

$$\tilde{E}_R = E_0 e \left[-i(\omega + \Delta\omega)t \right] e \left(-\frac{bt}{2} \right) \quad (1.39)$$

Noting that wave frequency doesn't change before and after reflection, the frequency shift $\Delta\omega \approx 0$.

Thus, the effect of the metal surface on an emitter is only the change of reflection wave. The effect of metal on decay rates is given by:

$$\frac{b}{b_0} = \frac{\tau_0}{\tau} = 1 + \frac{3qn_1^2}{2\mu_0k_1} \text{Im}(\tilde{E}_R) \quad (1.40)$$

where q is the quantum yield, k_l is the wavevector of the dielectric material, and n_l represents the refractive index of environment of the emitter. We can even use equation (1.40) to calculate relative decay rate for TE and TM polarizations:

$$\begin{aligned} \frac{b_{TM}}{b_0} &= 1 + \frac{3}{4}q \text{Im} \int_0^\infty \left[(1-\mu^2)r_{12}^{TM} + r_{12}^{TE} \right] e(-2l_1k_1d) \frac{\mu}{l_1} d\mu \\ \frac{b_{TE}}{b_0} &= 1 - \frac{3}{2}q \text{Im} \int_0^\infty r_{12}^{TM} e(-2l_1k_1d) \frac{\mu^3}{l_1} d\mu \end{aligned} \quad (1.41)$$

The reflection coefficient between dielectric and metal, r_{12}^{TE} and r_{12}^{TM} , can be calculated from Fresnel equations:

$$\begin{aligned} r_{12}^{TE} &= \frac{l_1 - l_2}{l_1 + l_2} \\ r_{12}^{TM} &= \frac{\epsilon_{r1}l_2 - \epsilon_{r2}l_1}{\epsilon_{r1}l_2 + \epsilon_{r2}l_1} \end{aligned} \quad (1.42)$$

here the amplitude of wavevector in material i direction is denoted as l_i . The values of l_1 and l_2 are given by:

$$\begin{aligned} l_1 &= -\sqrt{(1-\mu^2)}i \\ l_2 &= -\sqrt{(\epsilon_{r2}/\epsilon_{r1} - \mu^2)}i \end{aligned} \quad (1.43)$$

The total decay rate of the emitter above a metal mirror has drastic differences with that of in the absence of a mirror, and is described by:

$$b = b_{TE} + 2b_{TM} \quad (1.44)$$

It is difficult to figure out the factor that determine the quenching or radiation of the whole system. Far field radiation will arise as a result of the integral of dipole moment, μ , from 0 to 1, while the integral from 1 to infinity leads to nonradiative paths. The created field frequency will match surface plasmons when μ is integrated at 1. These results well interpret the dominating nonradiative fields when the emitter is near the metal surface.

Now we consider the emitter is placed in the proximity of the metal surface, the fluorescence rate γ_{em} is determined by excitation rate γ_{exc} and its quantum yield η :

$$\begin{aligned}\gamma_{em} &= \gamma_{exc} \eta \\ \eta &= \frac{\gamma_{rad}}{\gamma_{tot}}\end{aligned}\tag{1.45}$$

where γ_{rad} and γ_{tot} are the radiative rate and total rate of the emitter, respectively. Here the nonradiative rate $\gamma_{nonrad} = \gamma_{tot} - \gamma_{rad}$ is dominant when the emitter is in close proximity due to the enhanced quenching rate γ_{quench} .

For a vertical dipole placed on top of a metal surface with a separation of d , the quenching rate γ_{quench} boosts as the dipole approaches the metal surface[41]:

$$\gamma_{quench} = \frac{3}{8\epsilon_m (kd)^3} \text{Im}\left(\frac{\epsilon_{metal} - \epsilon_m}{\epsilon_{metal} + \epsilon_m}\right)\tag{1.46}$$

The cubic scaling of the distance d indicates the boosting quenching rate as $d \rightarrow 0$.

1.3.3 Localized Surface Plasmons

There are two distinct classifications of SPs known to exist: surface plasmon polaritons (SPPs) and localized surface plasmons (LSPs), depending on the geometry shown in Fig. 1.9. As

mentioned above, SPPs are driven at the interface of metal and dielectric, and decay exponentially away from the interface. In contrast, LSPs is a non-propagating SPs excitations resulting from a subwavelength conductive nanoparticle coupled to a nonevanescant propagating light field[42]. The LSPs can be generated both inside and at the vicinity of nanoparticles when they are resonantly excited by an electromagnetic field. The frequency and magnitude of the LSPs can be feasibly tuned by the geometry or composition of nanoparticle and the surrounding environment[43].

Fig. 1.9 Schematic illustration of SPs and LSPs together their corresponding dispersion relations. (a) and (b) are collective displacement of the electron charge cloud with SPs (a) and LSPs (b). Typical dispersion relations of SPs and LSPs. Adapted from REF[44], © 2011 Macmillan Publishers Limited.

Noble metal nanoparticles with subwavelength scale can support LSPs when the incident light is resonantly coupled with continuous electron bands (Fig. 1.9). Upon resonant excitation of a metal particle whose radius, r , is much smaller than the wavelength of incident light, the oscillation of conduction electron will be triggered by the oscillating electromagnetic field. This effect results in the buildup of polarization charges on the metal surface which can restore force for a plasmon frequency resonance. In the case of a well isolated spherically-shaped nanoparticles, the dipole oscillation contributes to the scattering C_{sca} and extinction cross sections, C_{ext} (absorption plus scattering), and it can be given by solving Maxwell's equations by a series expansion of the involved fields into spherical harmonic wave equations. For a spherical nanoparticle with radius r and refractive index n_p embedded into a surrounding medium with refractive index n_m , the cross section of scattering and extinction can be calculated[45]:

$$\begin{aligned} C_{sca} &= \frac{2\pi r^2}{x^2} \sum_{l=1}^{\infty} (2L+1) (|a_L|^2 + |b_L|^2) \\ C_{ext} &= \frac{2\pi r^2}{x^2} \sum_{l=1}^{\infty} (2L+1) \text{Re} \{ |a_L|^2 + |b_L|^2 \} \end{aligned} \quad (1.47)$$

here $x = \frac{2\pi}{\lambda} n_m r$ and λ denotes the interaction wavelength between the nanoparticle and light. And

the coefficients a_L and b_L are extracted from the Riccati-Bessel functions:

$$\begin{aligned} a_L &= \frac{m\psi_L(mx)\psi_L'(x) - \psi_L'(mx)\psi_L(x)}{m\psi_L(mx)\xi_L'(x) - \psi_L'(mx)\xi_L(x)} \\ b_L &= \frac{\psi_L(mx)\psi_L'(x) - m\psi_L'(mx)\psi_L(x)}{\psi_L(mx)\xi_L'(x) - m\psi_L'(mx)\xi_L(x)} \\ m &= n_p / n_m \end{aligned} \quad (1.48)$$

with

$$\begin{aligned}\psi_L(x) &= \sqrt{\frac{\pi x}{2}} J_{L+\frac{1}{2}}(x) \\ \xi_L(x) &= \sqrt{\frac{\pi x}{2}} (J_{L+\frac{1}{2}}(x) + iY_{L+\frac{1}{2}}(x))\end{aligned}\tag{1.49}$$

here the coefficients J_L and Y_L are functions of the particle size and λ in terms of Riccati-Bessel functions. The index L is the order of the partial waves, and the scatter and extinction cross section are composed of spherical multipole excitations from the lowest dipole ($L=1$) and quadrupole ($L=2$) modes to higher order multipoles.

Particularly, for small nanoparticles with $r \sim 10$ nm, only the lowest dipolar ($L=1$) and quadrupolar ($L=2$) modes contribute significantly to the solution, then equation (1.47) can be simplified as:

$$\begin{aligned}C_{ext} &= \frac{24\pi^2 r^3 \epsilon_m^{3/2}}{\lambda} \frac{\epsilon_i}{(\epsilon_r + 2\epsilon_m)^2 + \epsilon_i^2} \\ \epsilon_{metal} &= \epsilon_r + i\epsilon_i\end{aligned}\tag{1.50}$$

The SPs is excited when $\epsilon_r = -2\epsilon_{metal}$, for small ϵ_i . The equation (1.47) is applicable to spherical nanoparticles, C_{ext} of other various shapes can also be theoretically calculated. For example, the C_{ext} for metal nanorods can be expressed as:

$$C_{ext} = \frac{2\pi V}{3\lambda} \epsilon_d^{3/2} \sum_j \frac{(1/P_j^2) \epsilon_i}{\left(\epsilon_r + \frac{1-P_j}{P_j} \epsilon_m \right)^2 + \epsilon_i^2}\tag{1.51}$$

where V denotes the volume of gold nanorod, and P_j is the depolarization factor nanorod. These depolarization factor for the elongated nanorod are determined by:

$$P_{length} = \frac{1-e^2}{e^2} \left(\frac{1}{2e} \ln \left(\frac{1+e}{1-e} \right) - 1 \right) \quad (1.52)$$

$$P_{width} = \frac{1-P_{length}}{2} \quad (1.53)$$

where e is the nanorod ellipticity and described as:

$$e^2 = 1 - \left(\frac{length}{width} \right)^{-2} \quad (1.54)$$

With the equations above, the extinction properties of gold nanorods can be described for any aspect ratio. In addition, aspect ratio is the relevant figure of merit for significant changes in extinction bands, since the extinction also depends on the surrounding medium and materials properties.

Now we consider another factor known as the polarizability, α , which describes the distorted response of the conduction electrons to the external magnetic light field:

$$\alpha(\lambda) = 4\pi\epsilon_d(\lambda)r^3 \frac{\epsilon_{metal}(\lambda) - \epsilon_d(\lambda)}{\epsilon_{metal}(\lambda) + 2\epsilon_d(\lambda)} \quad (1.55)$$

At resonance condition $\epsilon_{metal}(\lambda) + 2\epsilon_d(\lambda) = 0$, the maximum polarizability is reached. This means the oscillating field is tightly confined around the nanoparticle and the polarization inside metal is also greatly enhanced, which enables ultra-strong interaction between light and matter with an ultra-small mode volume.

Fig. 1.10 Illustration of the quality factor of an optical cavity against its effective volume. The green arrow highlights strong coupling regime. Adapted from REF[46], © 2016 Macmillan Publishers Limited.

In summary, as shown in Fig. 1.10, the photonic crystals and dielectric resonators possess high quality factor but large mode volumes, which are suitable for the large-scale light source like perovskite film and quantum wells. In contrast, the volume can be dramatically scaled down in plasmonic nanocavities even though the quality factor is not so high. This small nanocavities can boost plenty of fascinating quantum phenomena when coupled with small light sources such as photonic emitters in monolayers and flakes.

1.4 Motivation and Layout of Dissertation

Coupling the energy transition of photon emitters to confined electromagnetic field in optical cavities could open up numerous applications in photonics and solid-state physics. The optical cavities can manipulate the photonic environment of photonic emitters and the interaction between

them results in weak coupling and strong coupling. In weak coupling regime, the spontaneous emission is strongly modified with enhanced light extraction of emitters, well known as Purcell effect. However, more profound effects are produced in strong coupling regime: new eigenstates with half-light and half-matter characters. These two regimes are distinguished by the coupling strength, g , which scales as $g \propto \sqrt{N/V}$, where N is the number of excitons involved in the interaction and V is the effective mode volume. The small-scaled optical cavities can increase the coupling strength and boost light-matter interaction. Although the decreased number of exciton N can reduce the coupling strength, approaching the limit of interaction between single photon emitter with optical electromagnetic mode is of great interest due to its potential applications in quantum communication[11, 18] and quantum networking[9, 10]. Here we investigated the light-matter interaction by coupling photon emitters with photonic and plasmonic cavities. Photon emitters experienced a photonic environment change from broadband confinement in photonic crystals to extreme field confinement in gap plasmonic nanocavities. By scaling down the size of the cavity volume from micrometers to nanometers, we successfully manipulate light emission with high extraction in photonic crystals at weak coupling regime and strong light-matter interaction in plasmonic nanocavities. Finally, we also created bright color centers in hexagonal boron nitride monolayers with laser ablation and single photon emission is further demonstrated. We then coupled the single photon source in hexagonal boron nitride with plasmonic nanocavities and observed modified spontaneous emission.

Chapter 2 gives a brief introduction about fabrication, simulation and characterization methods we used in the thesis. Fabrication techniques including electron beam lithography and chemical vapor deposition, and characterization methods such as ellipsometry and atomic force microscopy are described.

Chapter 3 discusses simultaneous inhibition and redistribution of light energy in perovskite PhCs. We first fabricated PhCs structures directly in perovskite film using electron beam lithography and reactive ion etching techniques. The perovskite PhCs demonstrated enhanced light emission with high extraction efficiency and slower decay in lifetime, as a result of photonic bandgap effect.

In chapter 4, we coupled MoS₂ monolayer with plasmonic gap nanocavities. In this study, we successfully observed a continuous transition from weak coupling to strong coupling between excitons in MoS₂ monolayer and highly localized plasmons in ultra-compact nanoantenna. Numerical calculations quantify the relation between coupling strength, mode volume and spacer thickness, and reveal the transition between weak coupling and strong coupling in nanocavities.

In chapter 5, we report bright and localized luminescent centers can be engineered in hBN monolayer and flakes using laser irradiation. Remarkably, the color centers in hBN flakes exhibit cleaner single photon emissions with $g^{(2)}(0)$ ranging from 0.20 to 0.42 at room temperature, a narrower line width of 1.4 nm and higher brightness compared to monolayers.

Chapter 6 discusses the conclusion of this thesis.

Chapter 7 outlines future works and direction.

Chapter 2 Experimental Methods

2.1 Fabrication Methods

2.1.1 Electron Beam Lithography

Fig. 2.1 Structure of a typical EBL system.

Electron beam lithography (EBL) refers to a specialized technique to create complex nanostructures with the practice of a tightly focused electrons beam. A typical EBL is usually built up with the following parts (Fig. 2.1): 1) an electron source; 2) an electron focusing system; 3) a mechanical positioning system; 4) a sample replacement chamber; 5) a computer for control. The electron beams are generated from an electron gun and then reshaped by electrode lens on the sample with an extremely small spot. The drawing of pattern for lithography is transferred from hard disc to the beam blanking and deflection control system by high speed data processing system. Subsequently, the combined precise movement of electron beam and sample stage starts to draw the designed by switching on and off the electron beam.

The operation of EBL consists of several procedures. An electron sensitive resist film is spin coated on the sample and utilized to record the pattern by changing the solubility and molecular structure of resist under electron exposure. Following exposure to electrons, the resist is developed in a solvent to selectively remove either exposed or nonexposed area of the resist. After developing, the patterned resist on the surface of sample can be used as a binary mask to transfer the pattern into useful mediums. Fig. 2.2 demonstrates the two typical pattern transfer techniques: patterning transfer by etching and lift off. The first is etching materials down with patterned resist as a mask while the second involves an inverse pattern in the useful medium.

Fig. 2.2 Schematic of two typical pattern transfer methods.

2.1.2 Reactive Ion Etching

Reactive ion etching (RIE) refers to a dry etching technique which utilizes reactive ion bombardment to etch down materials. When strong RF electromagnetic field is applied to the electrode, plasma is generated. The ionized gas results from the oscillation of electric field,

creating reactive plasma. Etching conditions in the chamber can be adjusted based on RF power, pressure and gas flow.

2.1.3 Electron Beam Evaporation

Electron beam evaporation (EBE) is a thin film deposition process in which the target anode is thermally vaporized by electron beam. In EBE system, a high vacuum is required to reduce the obstacle of electrons from a charged tungsten filament to target in crucible (Fig. 2.3). This process consists of two main parts: the electron gun, which is utilized to generate the electron beam, and the crucible section which holds the target materials. Multiple types of electron beam sources can be used to sequentially evaporate various target materials for multilayers depositions. The high voltage is applied to accelerate the generated electron beam and direct the beam towards evaporation materials in a curable. Upon striking, the interactions between electron beam and evaporation materials convert the energy of electrons into thermal energy to heat up target materials. Once the interactions are sufficient enough, the high temperature and vacuum lead to the evaporation of target materials. Precise thickness control of deposition can be realized by integration of real time optical monitoring and control hardware or software for single and multiple layer evaporation.

Compared with other deposition methods, the deposition rate of EBE is high and controllable. The directly heating efficiently promotes the utilization efficiency of target materials. More importantly, the evaporation of metal and metal oxides can be possible in EBE, which, however, is difficult with other methods.

Fig. 2.3 Schematic illustration of the EBE system.

2.1.4 Atomic Layer Deposition

Atomic layer deposition (ALD) is a surface controlled thin film deposition technique which involves a sequential one atomic layer process. Layers are slowly deposited on the surface of wafer during the reaction between precursors. The uniformity of the surface is optimized with low pin hole and particle levels. Not only does ALD offer precise thickness control with excellent uniformity, but the flexibility of unique deposition environment benefits a wide range of applications.

Basically, there are 4 steps involved during atomic layer deposition for one cycle, as shown in Fig. 2.4. The synthesis of Al_2O_3 layer from the reaction between trimethylaluminum (TMA) and water

is one of the best known ALD fabrications. The first step is dosing the wafer with a precursor vapor of TMA in a chamber, which is absorbed on wafer surface with self-limiting reactions. After this, the redundant precursor is purged out of chamber. Then the sample surface is oxidized, and the surface ligands are removed by low damage oxygen plasma. The limited surface ligands make this reaction also self-limiting process. Finally, the chamber is purged to clean all residual precursors. By varying the number of cycles, the process is repeated on demand to reach required layer thickness.

Fig. 2.4 Schematic illustration of ALD for one cycle.

2.1.5 Chemical Vapor Deposition

Chemical vapor deposition (CVD) of two dimensional (2D) materials has laid a foundation for preparation of large area 2D materials[47, 48]. Since the major breakthrough of CVD grown graphene, CVD has demonstrated its flexibility in the synthesis of various ultrathin materials, such as transition metal dichalcogenide (TMD) monolayers[48] and hexagonal boron nitride (hBN)[49]. Here we mainly discuss the details of MoS₂ monolayer synthesis using CVD method, as shown in Fig. 2.5. The two steps synthesis process in Fig. 2.5a involves the growth of multilayers MoS₂ by annealing (NH₄)₂MoS₄ at 500 °C with Ar/H₂ protection followed by sulfurization at 1000 °C[50].

The MoS₂ layers are obtained with a chemical reaction $(\text{NH}_4)_2\text{MoS}_4 + \text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{S} + \text{MoS}_2$.

The crystallinity of MoS₂ domain is improved by the second annealing at 1000 °C.

Fig. 2.5 Ultrathin TMD monolayers grown by CVD. (a) Schematic of MoS₂ monolayer deposited by two step thermolysis. (b) Schematic illustration of MoS₂ growth from single monolayer to multilayers. (c) Alternative method for the MoS₂ monolayer synthesis using MoO₃ and S powders. (d) Illustration of wafer scale MoS₂ monolayers and their transfer processes. Adapted from REF[48], © 2013 Macmillan Publishers Limited.

Monolayer MoS₂ can also be deposited based on the sulfurization of Mo metal[51], as shown in Fig. 2.5b. Another alternative method for MoS₂ monolayer growth is based on the gas phase reaction between MoO₃ and S powders[52]: $\text{MoO}_3 + x/2\text{S} \rightarrow \text{MoO}_{3-x} + x/2\text{SO}_2$ and $\text{MoO}_2 + (7-x)/2\text{S} \rightarrow \text{MoS}_2 + (3-x)/2\text{SO}_2$. There is still a challenge to synthesize wafer scale MoS₂ monolayer using this method (Fig. 2.5c). A different strategy to grow wafer scale MoS₂ is using the same chemicals and sulfurizing MoO₃ films to obtain large area MoS₂ layers[53] (Fig. 2.5d).

2.2 Characterization Methods

Various materials with unique optical properties can be synthesized using the above fabrication methods. Depending on the situation, specialized optical characterization methods provide insights of materials features. The thickness and optical constants can be obtained by atomic force microscopy and ellipsometry measurements. The properties of photoluminescent materials can be even understood by steady state photoluminescence, time resolved photoluminescence and antibunching measurements.

2.2.1 Atomic Force Microscopy

Atomic force microscopy (AFM) is a high-resolution scanning probe microscopy of which the interatomic force can image the surface topography of samples at the atom scale. AFM is a multifunctional technique which can determine plenty of material features including resistance, roughness, electrical forces, conductivity and friction. Compared with scanning tunneling microscopy which can only image conducting materials, AFM is developed to overcome this shortcoming to image almost any type of surface, such as glass, polymers and ceramics.

Fig. 2.6 Schematic diagram of the AFM system using beam deflection detection.

As shown in Fig. 2.6, a sharp tip at the end of cantilever is used in AFM to scan over the sample surface. This cantilever is typically made from silicon or silicon nitride and the curvature radius of the tip is on the magnitude of nanometers. The force between the tip and the sample surface is not measured, but calculated by the deflection of cantilever based on Hooke's Law and the stiffness of the lever. Depending on the application, the AFM can be adjusted into imaging mode, noncontact mode, contact mode and tapping mode.

2.2.2 Ellipsometry

Ellipsometry is a materials evaluation technique to measure the optical properties of thin films without damage to the sample surface. Ellipsometry measures the generated polarization changes when a light is reflected from the specular surface of a sample of interest. This sensitive measurement offers unequalled insights on surface roughness, thin film thickness, chemical composition and optical constants. There are five steps entailed in an ellipsometry measurement (Fig. 2.7): 1) a polarized light beam generated using polarizer and compensator; 2) the reflection

of light beam on the surface of a sample leading to the change of polarization state 3) collection and analysis of the reflected light beam; 4) determination of the reflection parameters from the comparison of polarization states before and after reflection; 5) extraction of sample properties from modelling. Most modelling is based on the assumption that the sample consists of well-defined layers which have continuous and optically isotropic surface.

Fig. 2.7 Schematic of an ellipsometry setup.

The measured signal of reflection is the change of polarization state resulting from the interaction between incident light and the sample surface of interest. The outcome is quantified in the terms of amplitude ratio, Ψ , and the phase shift, Δ . The incident light can be decomposed into s and p components where the oscillating electric field is perpendicular (s) and parallel (p) to the plane of incidence. The relation between amplitude ratio, Ψ , and the phase shift, Δ , can be parameterized using the amplitudes of s (r_s) and p (r_p):

$$\rho = \frac{r_p}{r_s} = \tan \Psi \cdot e^{i\Delta} \quad (2.1)$$

Here, ρ is the complex reflectance ratio of r_p over r_s . The measured Ψ and Δ can be used to probe the optical properties of materials by choosing apposite models.

Since ellipsometry measures the complex relation of two parameters rather than the independent value of either, it is very sensitive, accurate and reproducible to achieve angstrom resolution. More importantly, this non-destructive and non-contact technique can be applicable to solid and liquid samples with single or multiple layer.

2.2.3 Steady State Photoluminescence

Fig. 2.8 Schematic illustration of steady state photoluminescence setup

Steady state photoluminescence employs laser excitation and far field detection of emission signal, which has been widely exploited in various scientific disciplines in physics. In this thesis, we use the spectrometer from Edinburgh Instruments to measure steady state photoluminescence. The schematic illustration of the photoluminescence measurement principle is shown in Fig. 2.8.

Suitable Photomultiplier Tubes (PMTs) detector is used to detect emitted photons in high sensitivity and accuracy in the acquisition of spectral data.

The pulse laser is focused by an objective and excites sample to generate scattered and reflected photon emissions. The reflected excitation is then distinguished from emission using a long-pass filter in front of the spectrometer. The focused laser spot size, D , is determined by the laser wavelength λ_{laser} and the numerical aperture NA of the objective (Rayleigh criteria):

$$D = 1.22 \frac{\lambda_{laser}}{NA} \quad (2.2)$$

For our laboratory situation, the laser with $\lambda_{laser} = 532 \text{ nm}$ and an objective with $NA=0.95$ are used, then the spot radius is limited to $\sim 342 \text{ nm}$.

2.2.4 Time Resolved Photoluminescence

The photoluminescence lifetime, as an intrinsic characteristic of fluorescence species, can offer insights into the physical dynamic processes of excited state. Time resolved photoluminescence (TRPL) is an experimental tool to study the spectral and temporal electronic deactivation processes of photon emission from a sample. More specifically, when the electron-hole pairs are generated by a pulse of light, before decaying back to lower energy states, they will stay in high energy states for a specific time known as the lifetime. These subsequent recombination of electron-hole pairs results in the photon emissions. Lifetime, as a characterization technique by measuring the optical spectrum as a function of time, provides a tool to analyze specific radiation states of photon emission.

Time correlated single photon counting (TCSPC) is a popular technique used for TRPL measurement with high sensitivity and accuracy. TCSPC reconstructs the lifetime decay over

many events as a function of the time difference between a laser pulse excitation source (START) and the observation of the first emitted photon on the photodetector (STOP), as shown in Fig. 2.9a. As shown in Fig. 2.9b, the probability density is proportional to the photoluminescence intensity. Statistical nature of the kinetic process of photoluminescence decay is reconstructed by the collection of repeating data.

Fig. 2.9 The operating principle of TCSPC. (a) Emissive photons are detected over a time. (b) The decay curve is a histogram resulting from the collection of repeated sweeps.

The electronics is the relevant figure of merit for achieving high lifetime resolution, since it is also dependent on the excitation source and the PMT used. The instrument response function (IRF) is a factor to evaluate the timing precision of the TRPL measurement, and is determined by the width of the laser pulse and the PMT response time.

2.2.5 Photon Correlation

The nature of a light source can be determined by recording time intensity correlations between detectors. The first order correlation function, $g^{(1)}(\tau)$, is defined as:

$$g^{(1)}(\tau) = \frac{\langle E^*(t)E(t+\tau) \rangle}{\langle E^*(t)E(t) \rangle} \quad (2.3)$$

in which $E(t)$ is the sum of amplitude of optical field. The trajectory of the PL intensity can be easily retrieved from spectral analysis in first order correlation function. However, to access the quantum features of emitters, second order correlation function, $g^{(2)}(\tau)$, is constructed to investigate the quantum nature of single photon sources:

$$\begin{aligned} g^{(2)}(\tau) &= \frac{\langle E^*(t)E^*(t+\tau)E(t+\tau)E(t) \rangle}{\langle E^*(t)E(t) \rangle \langle E^*(t+\tau)E(t+\tau) \rangle} \\ &= \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle} \end{aligned} \quad (2.4)$$

here $I(t)$ is the intensity of the electric field at time t . In case of chaotic light, the random phases are reorganized with no cross terms with $I(t) = I(t+\tau)$, which results in:

$$\begin{aligned} g^{(2)}(\tau) &= \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle} \\ &= \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2} \end{aligned} \quad (2.5)$$

Based on quantum mechanics, there will be a dip to zero at zero delay with $g^{(2)}(0) = 0$. In quantum theory, the operator of photon number is determined by photon creation operator ($\hat{a}^\dagger$) and annihilation operator ($\hat{a}$): $\hat{n} = \hat{a}^\dagger \hat{a}$, where $\hat{a}^\dagger$ and $\hat{a}$ are given by:

$$\begin{aligned}\hat{a}^\dagger |n\rangle &= (n+1)^{1/2} |n+1\rangle \\ \hat{a} |n\rangle &= (n)^{1/2} |n-1\rangle\end{aligned}\tag{2.6}$$

Then the $g^{(2)}(\tau)$ can be determined with these operators:

$$g^{(2)}(\tau) = \frac{\langle \hat{a}_3^\dagger(t) \hat{a}_4^\dagger(t+\tau) \hat{a}_4(t+\tau) \hat{a}_3(t) \rangle}{\langle \hat{a}_3^\dagger(t) \hat{a}_3(t) \rangle \langle \hat{a}_4^\dagger(t+\tau) \hat{a}_4(t+\tau) \rangle}\tag{2.7}$$

at zero delay time, $g^{(2)}(0)$ can be expressed as:

$$g^{(2)}(0) = \frac{\langle \hat{a}_3^\dagger(t) \hat{a}_4^\dagger(t) \hat{a}_4(t) \hat{a}_3(t) \rangle}{\langle \hat{a}_3^\dagger(t) \hat{a}_3(t) \rangle \langle \hat{a}_4^\dagger(t) \hat{a}_4(t) \rangle}\tag{2.8}$$

The input states of the light beam can be described using arbitrary: $\Psi = |\Psi_1, 0_2\rangle$ where Ψ_1 denotes the arbitrary state at port 1 and $|0_2\rangle$ is the vacuum at port 2. Then the $g^{(2)}(0)$ in equation (2.8) can be simplified as:

$$\begin{aligned}g^{(2)}(0) &= \frac{\langle \Psi_1 | \hat{n}_1(\hat{n}_1 - 1) | \Psi_1 \rangle / 4}{\left(\langle \Psi_1 | \hat{n}_1 | \Psi_1 \rangle / 2 \right)^2} \\ &= \frac{\langle \hat{n}(\hat{n} - 1) \rangle}{\langle \hat{n} \rangle^2}\end{aligned}\tag{2.9}$$

and by replacing the operators with photon number state and then we have:

$$g^{(2)}(0) = \frac{n(n-1)}{n^2} \quad (2.10)$$

For an ideal single photon emission where only one photon is emitted with $n=1$, $g^{(2)}(0) = 0$, resulting in an antibunching dip in correlation function plot, which is the signature of quantum emission from single photon source.

Considering N independent quantum sources [54] with PL intensity of q_i and a classical light source C with the intensity of c . This classical light source mainly originates from the background fluorescence. The $g^{(2)}(0)$ can be rewritten as:

$$g^{(2)}(0) = \frac{c^2}{R^2} + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left(\frac{q_i q_j}{R^2} \right) + 2 \sum_{i=1}^N \frac{c q_i}{R^2} \quad (2.11)$$

in which $R = \sum_{i=1}^N q_i + c$ is the total light intensity. Then we pay attention to the two typical experimental conditions.

The first condition is that there are two single photon sources without classical background. Under this condition, the equation (2.11) changes to:

$$g^{(2)}(0) = \frac{2q_1 q_2}{(q_1 + q_2)^2} \quad (2.12)$$

In case of $q_1 = q_2$, the equation (2.12) is bounded by $g^{(2)}(0) = 0.5$. This is the origin of the definition that the experimental single photon emission from individual quantum source yields $g^{(2)}(0) < 0.5$.

Another situation is the individual single photon source with a classical background light. Then equation (2.11) becomes:

$$g^{(2)}(0) = \frac{2q_1c + c^2}{(q_1 + c)^2} \quad (2.13)$$

Different from the equation (2.12), this expression is bounded by $g^{(2)}(0) = 1$ in the case of $q_1 \ll c$.

And even if $q_1 = c$, we still can get $g^{(2)}(0) = 0.75$. Then we can draw a conclusion that the depth of an antibunching dip is more pronouncedly affected by the classical background light source than a second individual quantum source.

2.5.6 Hanbury Brown and Twiss setup

Fig. 2.10 Schematic illustration of HBT setup used to probe single photon sources

The second order correlation function can be measured using Hanbury Brown Twiss (HBT) system as depicted in Fig. 2.10. The PL signal is divided equally into two beams by a 50/50 beam splitter. The two outputs from the beam splitter are focused on two silicon avalanche photodiodes (ADP) for detection. The coincident card records the time delay between inputs pulses. A histogram of

coincidences is built from the collection of sweeps and reconstructs the second order correlation function.

Fig. 2.11 Two examples of a second-order correlation function of the antibunched light from a perfect single emitter excited continuous wave laser (a) and pulse laser (b).

Fig. 2.11 shows two antibunching curves from an ideal individual single photon source measured using HBT setup. At zero delay time, $g^{(2)}(0)$ decreases to zero under continuous excitation and the zero-delay peak is suppressed in pulsed mode, which indicates single photon emission.

Chapter 3 Light Manipulation in Perovskite Photonic Crystals

All inorganic cesium lead halide perovskite semiconductors exhibit great potential for nanolasers, light emitting diodes and solar cells due to their unique properties including low threshold, high quantum efficiency and low cost. However, the high material refractive index of perovskite semiconductors hinders light extraction efficiency for photonic and illumination applications. In this chapter, we demonstrate high light extraction efficiency achieved in $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ two dimensional photonic crystals in weak coupling regime. The perovskite photonic crystals exhibit both emission rate inhibition and light energy redistribution simultaneously. Such a combination of inhibiting undesirable emission with redistributing light energy into useful modes offers a new promising approach in various applications for perovskite, including solar cell, displays and photovoltaics.

3.1 Motivation and Introduction

All inorganic halide perovskites possess a unique combination of intriguing properties in a broad range of optoelectronic devices, such as high carrier mobility, tunable emissions and economic cost for commercial use[55]. Among these features, bright and tunable PL emissions and flexible fabrication methods highlight perovskite's potential in imaging, lasers, and even light emitting diodes(LEDs)[56-63].

Perovskite possesses a unique crystal structure of ABX_3 where the cations A and B are bound to an anion X. Methylammonium (MA) lead trihalide perovskites with chemical composition of $\text{CH}_3\text{NH}_3\text{PbX}_n\text{Y}_{3-n}$ are the most explored materials in optics and electronics. The inorganic-organic hybrid perovskite has spectrally tunable direct bandgap by controlling the composition of halides.

Their emission wavelength can be flexibly tuned from 390 nm to 820 nm, which has brought about breakthroughs in photovoltaic[64].

The organic composition of MA makes this inorganic-organic hybrid perovskite sensitive to air and illumination, which greatly limits its performance in optoelectronics device. All inorganic perovskite CsPbX_3 has recently been extensively investigated. These perovskites demonstrate a wide emission range from 410 nm to 700 nm with narrow bandwidth. In addition to perovskite thin film fabrication, large single crystal perovskites from solution-based growth has been also reported. The most conspicuous advantage of single crystal perovskites is that it offers much lower defect density in the bulk, which can largely suppress non-radiative pathways[65].

Early in the 1900s, people have demonstrated organic conjugated polymer LEDs and lasers with solution processed semiconductors[66, 67]. Over several decades later, promising contenders have been well developed including organic semiconductors, colloidal quantum dots and now perovskites. The optical performance of perovskite film is largely dependent on the film formation method. Additionally, the external collection efficiency of generated light is greatly hindered by the large internal reflection in perovskite thin films due to their high refractive index[68]. Hence, most of the emitted light is coupled to in-plane guided modes in perovskites thin films, thereby serving as a fundamental limit for the light extraction efficiency in perovskite devices. Losses in LED and noises in lasers have been attributed to the uncoupled light emission[69, 70]. Therefore, increasing the extraction efficiency of useful modes while simultaneously inhibiting undesirable ones would make great improvements in perovskite devices.

2D photonic crystals have a periodic refractive index distribution which can control the propagation of light in the dielectric medium and enhance quantum efficiency with Purcell effect through the cavity[12, 71, 72]. The photonic crystals can be well designed to tune its bandgap to

spectrally overlap with that of the emission and penetrate through the whole device, eliminating 2D in-plane modes with PBG effect and thus extracting light emission out of plane with high collection efficiency[73-77].

In this chapter, we design and fabricate photonic crystals directly on $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ perovskite thin films by electron beam lithography and reactive ion etching (RIE). The photonic crystals structure exhibit strong light emission enhancement with a factor of 23.5 while their light emission rate is largely suppressed by 7.9 folds compared to the un-patterned area in the same sample. According to three-dimensional finite-difference time-domain (3D FDTD) simulations, the PL enhancement is attributed to the redistribution of light energy where most of in-plane spontaneous emission of guided modes are inhibited due to photonic crystals PBG effect, leading to the increase of extraction efficiency via out-of-plane modes. In addition, we also observed PL peak shifts from $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ perovskite photonic crystals with different lattice constants.

3.2 Methods

$\text{CsPbBr}_{2.75}\text{I}_{0.25}$ Thin Film Fabrication

$\text{CsPbBr}_{2.75}\text{I}_{0.25}$ solution was prepared by dissolving CsBr, CsI and PbBr_2 with a molar ratio of 0.75:0.25:1 in DMSO (0.5 M) and stirred at 100 °C till complete dissolution. $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ thin film was prepared by spin-cast precursor solution on SiO_2/Si wafer at 4000 rpm (acceleration: 1000 rpm/s) for the 30 s and blow- drying by N_2 in the last 15 s when sample was spinning[78], giving a thickness around 150 nm. The thin film was then annealed at 100 °C on hotplate for 15 min. The $\text{CsPbBr}_x\text{I}_{3-x}$ is relatively stable with the humidity and the sample can sustain of about one week in the open air[78]. The lithography process was performed in the vacuum condition while

we kept our samples in the vacuum desiccator directly after the fabrication. The measurement was performed at the same day.

Perovskite Photonic Crystal Fabrication

The perovskite thin film was spin coated with 200 nm electron sensitive 950 PMMA polymer and baked at 180 °C for 3 mins. Then, the PMMA polymer was exposed to electron beam writing (Raith EBPG5000) with 100 keV voltage and 1 nA beam current and developed in MIBK/IPA. The nanopatterns were then transferred into perovskite thin film by reactive ion etching (RIE Oxford Plasmalab80 System) with a gas mixture of SF₆ and Ar at 170 W forward power.

Optical Characterization

Absorption spectra of perovskite thin films were obtained using UV-VIS spectrometer (Shimadzu UV-2450), while the PL and lifetime measurements were carried out using free space home-built micro-PL setup at ambient environment at room temperature. A 355 nm pulse laser (VisUV, PicoQuant) with 15 ps linewidth and 10 MHz repetition rate was focused on samples with a microscope objective (Olympus 40x, NA = 0.65, focused laser beam diameter, ~ 1 μm). PL signal was collected by a Peltiercooled photomultiplier tube (Hamamatsu H7422 series) coupled with a grating spectrometer (Edinburgh Instruments F900 and Bentham TMS300) and the PL image was collected by a silicon charge coupled device (CCD). Time resolved PL measurement was performed using a time-correlated single-photon counting acquisition module (Micro Photon Devices MPD series) at selected peak wavelengths with a bandwidth of 20 nm.

Surface Characterization

LEO 1550 Gemini field emission scanning electron microscopy (FESEM) was used to obtain SEM images and the roughness of perovskite thin film was investigated by Bruker Dimension Edge Atomic Force Microscope.

Theoretical Simulations

Three dimensional (3D) finite difference time domain (FDTD) is carried out to theoretically analyze how spontaneous emission is modified and energy is redistributed in photonic crystals. The photonic crystals are modeled using the same structures in the experiment. In order to decrease the simulation time and avoid unnecessary reflection of light from the boundary of simulation region, Bloch, Bloch and perfectly matched layers are used for x, y and z boundaries, respectively. The simulation time was set as 1000 fs to allow for the decaying field to dissipate. The photonic bandgap was calculated using a dipole cloud analysis group to excite all modes of the system. The dipoles are randomly oriented and distributed to make sure all modes are excited even if one dipole is placed at a node. The bandstructure analysis was used to calculate the resonant frequencies over a range of k values. For the emission rate, we used perfectly matched layers for all boundaries and quantum efficiency analysis group. The dipoles are placed in the slab with random orientation and position. The light extraction efficiency of the structures is defined as the fraction of optical power emitted out of the layer that escapes into the air within a desired angle: $LEE = \frac{\gamma_{vertical}}{\gamma_{tot}}$. In order to

calculate the fraction of useful power that escapes from the slab, the far field projection analysis was used to integrate the far field distribution to get the energy of light in the air. The calculation was also performed without photonic crystals for reference and the results for photonic crystals slab were normalized by this reference. The optical constants of CsPbBr_{2.75}I_{0.25} perovskite thin films are obtained from spectroscopic ellipsometer and their detailed values are shown in Fig. 3.3.

3.3 Results and Discussion

3.3.1 Perovskite Film Characterization

3.3.1.1 Surface and Optical Characterization

Fig. 3.1 Characterization of spin-cast $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ perovskite thin film on SiO_2/Si substrate. (a) Optical microscope image of $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ thin film on SiO_2/Si substrate. (b) AFM scanning image. The arithmetic average surface roughness is 15.0 nm. (c) Normalized absorption (dotted line) and PL spectra (solid line) of $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ (red) and CsPbBr_3 (blue) thin films.

The hybrid $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ perovskite thin film was spin cast on SiO_2/Si substrate with DMSO as host solvent (see Methods for full details). The CsPbBr_3 thin film is already known as a base in ultra-bright and highly efficient inorganic based perovskite light-emitting diodes with[79] or without nanostructures[80]. The as-prepared $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ thin film presents smooth surface with a roughness of 15 nm with a thickness of 150 nm, indicative of a good quality thin film. A rough

surface will benefit a high light extraction efficiency[54, 81], while the roughness can increase the difficulty of EBL processing. Here we choose perovskite film with 15 nm roughness as a trade-off between external quantum efficiency and photonic crystals fabrication. The $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ is chosen due to its larger Stokes shift than that of CsPbBr_3 , which enables the inhibition of self-absorption and simplifies photonic crystals design. Fig. 3.1c shows UV-Vis absorption and emission spectra of $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ and CsPbBr_3 . The maximum emissions ($\lambda_{\text{max}}^{\text{em}}$) occur at 549 nm and 525 nm, and absorption transition edges appear at 526 nm and 520 nm for $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ and CsPbBr_3 , respectively. The longer $\lambda_{\text{max}}^{\text{em}}$ and absorption edge of $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ result from phase transition due to the iodine dopant, which is consistent with those in literature[82-84].

3.3.1.2 Transmission of Perovskite Film

Fig.3.2 Transmission spectra of perovskite film. (a) Normalized transmission of the perovskite film. (b) Transmissions of the glass substrate.

We have measured the transmission spectra from the $\text{CsPbBr}_{2.75}\text{I}_{0.25}$ unpatterned film on a glass substrate. The transmissions were measured from 5 different locations across the sample. The transmission for the perovskite film is normalized to that of the glass substrate. As shown in Fig.3.2a, the free spectral range (FSR) for the perovskite transmission is generally very weak, with

a strong transmission dip around ~ 500 nm which is attributed to the perovskite absorption at 525 nm. The FSR of the perovskite film was found to be ~ 6 THz. In order to validate that the FSR correlates with the perovskite, we then measured the FSR associated with the glass substrate from the transmission across glass substrate (see Fig.3.2b). We found the FSR to be ~ 6 THz, which is qualitatively similar with that in perovskite film. We thus conclude that there is no Fabry-Perot reflection associated with multiple reflections inside the perovskite film. This is as expected from the ~ 15 nm roughness measured from our AFM measurements.

3.3.1.3 Optical Constants of CsPbBr_{2.75}I_{0.25} film

Variable angle spectroscopic ellipsometer (J. A. Woollam M-2000) was used to obtain optical constants of CsPbBr_{2.75}I_{0.25} thin films. Typically, the measured data is presented in a spectral range of 0.73~5.06 eV with various angles of incidence. To analysis ellipsometry spectroscopic data, B-splines optical model is used to fit the obtained Ψ and Δ to extract optical constants until lowest mean squared error (MSE) is achieved[85]. A B-spline model is defined as:

$$B_i^0(x) = \begin{cases} 0 & t_i \leq x \leq t_{i+1} \\ 1 & \text{otherwise} \end{cases} \quad (3.1)$$

$$B_i^k(x) = \left(\frac{x - t_i}{t_{i+k} - t_i} \right) B_i^{k+1}(x) + \left(\frac{t_{i+k+1} - x}{t_{i+k+1} - t_{i+1}} \right) B_{i+1}^{k+1}(x)$$

where k is the degree of the B-spline and the locations are knotted by the subscript i. Then the dielectric function can be determined by:

$$\varepsilon_2(\omega) = \sum_{i=1}^n c_i B_i^k(\omega) \quad (3.2)$$

$$\varepsilon_1(\omega) = \varepsilon_1(\infty) + \sum_{i=1}^n c_i \phi_i^k(\omega)$$

where

$$\phi_1^k(\omega) = \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' B_i^k(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (3.3)$$

Finally, the dielectric function is transformed into optical constants as shown in Fig. 3.3. And the MSE is 14.32.

Fig. 3.3 Frequency dependent optical constants of CsPbBr_{2.75}I_{0.25} thin films. (a) real and (b) imaginary parts of the refractive index.

3.3.2 Perovskite Photonic Crystals Characterization

3.3.2.1 Optimizing Photonic Crystals Quality

Fig. 3.4 Optimizing EBL dose to achieve high quality photonic crystals. (a) SEM image of perovskite photonic crystals exposed to various electron doses. SEM images of perovskite thin films with incomplete dose ($600 \mu\text{C}/\text{cm}^2$) exposure (b) optimal dose ($1100 \mu\text{C}/\text{cm}^2$) exposure (c) and excessive dose ($1600 \mu\text{C}/\text{cm}^2$) exposure.

We also tried to optimize the quality of photonic crystals by adjusting the electron dose during EBL exposure. And we found the optimal dose to achieve high quality perovskite photonic crystals is around $1100 \mu\text{C}/\text{cm}^2$, as shown in Fig. 3.4c.

3.3.2.2 Defect by Patterning

Fig. 3.5 EBL dose effect on perovskite films: (a) Optical microscopy image of four squares patterns by EBL processing. (b) Photoluminescence spectra and (c) time-resolved emission curves from different treatment doses. (d) PL integrated intensity and average lifetime as function of EBL dose.

In order to reveal the effect of electron beam on perovskite films, we prepared EBL exposed square patterns on PMMA coated perovskite films (Fig. 3.5a) and performed optical measurements on patterns and non-exposed perovskite films. PL intensity becomes lower with the increase of EBL dose, as shown in Fig. 3.5b. So, the observation of the intensity enhancement was pure by photonics effect. The photonic crystals do really enhance the extraction of the emission. For the emission lifetime, the decay curves were also fitted with three decay components (Fig. 3.5c). The fast and the second components of the decay curves are still around 1.5 and 4 ns, respectively (for different doses). The only change is the slow component. It becomes faster (50 to 30 ns) and more dominant (larger contribution) towards higher doses. However, the most important parts are the average lifetimes. At doses of 1100 $\mu\text{C}/\text{cm}^2$ and below, the average lifetime does not change much. At 1300 $\mu\text{C}/\text{cm}^2$, the average lifetime strongly fluctuates but it is still around 3.5 ns (much faster

than 20.97 from photonic crystals). So, the EBL processing may induce some defects which can create more non-radiative recombination paths and reduce the total emission rate (Fig. 3.5d). This is also confirmed by observed ~ 20 ns slow component in Table 3.1. To minimum the effect of EBL and avoid incomplete exposure, the fabrication of photonic crystal was performed at $1100 \mu\text{C}/\text{cm}^2$.

3.3.2.3 Photonic Crystals Quality

Fig. 3.6 Perovskite photonic crystals quality inspection. The distributions of air hole diameter (a) and lattice constant (b). (c) Cross-sectional SEM image of perovskite thin film. Scale bar: 100 nm. (d) Transmission spectra from perovskite photonic crystals, the shaded area indicates the photonic bandgap region.

Statistics analysis of fabricated photonic crystals in Fig. 3.6a and b show that the air hole diameter is around 181 ± 10 nm and the lattice constant is around 280 ± 8 nm. Cross-sectional SEM image in Fig. 3.6c shows that the thickness of perovskite thin film is around 150 ± 15 nm. The

transmission measurement in Fig. 3.6d was carried out by a home built optical setup with halogen lamp focused into the sample. The transmitted signal was directed into a grating and CCD sensor by an objective lens (100X, 0.9 NA). The transmission spectra were obtained by normalizing the signals from perovskite thin film without patterns. A suppression dip in transmission spectra was clearly observed which is related to PBG effect in photonic crystals.

3.3.2.4 Perovskite Photonic Crystals Design and Theoretical Analyses of PBG effects

Spontaneous light emission is usually manipulated by optical modes and photonic crystals offer an effective platform to control optical modes[86, 87]. The perovskite photonic crystals were achieved using EBL and RIE techniques (Fig. 3.7a and b). This fabrication is challenging as the perovskite materials are usually unstable as they are hygroscopic. However, here we chose all inorganic perovskite materials with the improvement in humidity stability[88]. Compared to focused ion beam lithography[89], we are able to make much larger structures with faster speed with EBL. The optical modes inside perovskite photonic crystals film can be categorized into two modes. First are guided modes, which confine light emission into perovskite thin films due to the high refractive index. Second are vertical modes, which can penetrate perovskite films and increase extraction efficiency. Generated spontaneous light emission can be coupled into both guided modes and vertical modes, and only the vertical modes contribute to useful energy while guided modes cause losses and noises. Thus, the total spontaneous emission rate (γ_{total}) can be expressed by[69]:

$$\gamma_{total} = \gamma_{guided} + \gamma_{vertical} \quad (3.4)$$

where γ_{guided} and $\gamma_{vertical}$ are the generated light emission rate for guided modes and vertical modes, respectively. For unpatterned perovskite films surrounded by air, emission is strongly confined

inside perovskite films ($\gamma_{guided} \gg \gamma_{vertical}$), leading to low extraction efficiency. However, when emission frequency is overlapped with PBG in an incorporated 2D photonic crystals, guided modes in films can be greatly inhibited with slower emission rate and most of emitted light emission is then redistributed into vertical modes with higher extraction efficiency. This implies that both reduction of spontaneous emission rate in guided modes and redistribution of light energy can appear simultaneously in photonic crystals. To further investigate light emission inhibition and energy redistribution in perovskite photonic crystals, 3D FDTD simulations are carried out to calculate spontaneous emission rate and light extraction efficiency, and the results are normalized with values from simulated unpatterned perovskite thin films. Fig. 3.7c illustrates the photonic bandgap structure of 2D photonic crystals. Fig. 3.7d shows that the light emission rate within photonic bandgap is decreased by around 16.7 times compared to that of unpatterned area. Meanwhile, light extraction efficiency within bandgap region is largely increased by around 32.0 folds (Fig. 3.7e), which results from the redistribution of light emission. Cross-sectional views of electric field distributions are shown in Fig. 3.7f), revealing how light is controlled by PBG effect in photonic crystals. Obviously, for emission wavelengths lying outside of photonic bandgap region, the light extraction efficiencies are much lower, indicating light emission is mostly confined inside guided in-plane modes. However, when the frequency overlaps with bandgap region, the emission rate of guided modes is greatly reduced ($\gamma_{guided} \sim 0$) and emission energy is largely emitted out at vertical direction.

Fig. 3.7 Perovskite photonic crystals design. (a) Schematic of perovskite photonic crystals. (b) SEM image of a perovskite 2D photonic crystals. Inset: top view of calculated electric field distributions in 2D photonic crystals at $a/\lambda = 0.53$. Scale bar: 200 nm. (c) Photonic band structure of 2D hexagonal lattice photonic crystals calculated using FDTD. (d) Calculation of spontaneous light emission rate for various frequency, normalized by unpatterned structure. (e) Calculated light extraction efficiency in the vertical direction as a function of frequency, normalized by unpatterned structure. (f) Calculated cross-sectional (x-z) electric field distributions, illustrating how light is redistributed by photonic crystals. The lattice constant 280 nm and air hole diameter 180 nm are used for the simulation. The thickness of perovskite is 150 nm.

3.3.2.5 Optical Performance of Perovskite Photonic Crystals

To quantify the performance of perovskite photonic crystals, detailed optical measurements were conducted on photonic crystals films with various lattice constants. As shown in Fig. 3.8a, perovskite photonic crystals demonstrated higher PL intensity than that from unpatterned area. The

PL intensity is greatly enhanced up to 23.5 folds in perovskite photonic crystals with a lattice constant of 282 nm compared to that of unpatterned area at the same pump energy density. Photonic crystals rectangular areas exhibit brighter emissions when excited with an unfocused laser (inset of Fig. 3.8a), which further proves the PL intensity enhancement. Notably, we also found small PL peaks shifted to shorter wavelengths from 550 nm in unpatterned perovskite to around 520 nm in photonic crystals areas. These shifts are attributed to the PBG effect in photonic bandgap structure and qualitatively agrees with the expectation from FDTD simulations. This kind of band edge effect contributes to unpolarized light emissions of photonic crystals samples even when excited with a polarized laser (Fig. 3.8b). Fig. 3.8c presents intensity-dependent PL decays fitted with three exponential functions for both perovskite photonic crystals and unpatterned samples. Clearly, the perovskite photonic crystals exhibit much slower decays compared to unpatterned films: 20.97 ns and 2.66 ns, respectively. The slower decays in perovskite photonic crystals are due to the inhibition of light emission at guided modes, resulting in the increase of lifetime. And the redistribution of light energy into vertical modes contribute the enhancement of PL intensity. These results are in good agreement with the simulation in Fig. 3.7 and both light emission inhibition and redistribution are experimentally realized as shown in Fig. 3.8d. Here, the photonic crystal with $a=282$ nm demonstrated the highest PL intensity while perovskite photonic crystals with $a = 260$ nm has the longest lifetime. This inconsistency mostly results from the difficulty of fabricating homogeneous perovskite films. Plenty of defects are induced into the film during spin coating and EBL processing (shown in Fig.3.5), which have significant influence on the performance of perovskite. Although this can make it difficult to compare the performance of photonic crystals with various lattice constants, it is still very clear that perovskite with photonic crystals structures demonstrated higher PL intensity and longer lifetime.

Fig. 3.8 Optical measurements of perovskite photonic crystals. (a) and (c): Steady state PL and time resolved PL spectrum from perovskite photonic crystals with lattice constants of 256 nm, 260 nm, 274 nm, 282 nm and without pattern, respectively., which are pumped by a focused laser beam with a diameter of $\sim 1 \mu\text{m}$. Inset of (a) shows photographic image from a sample with three different lattice constants photonic crystals excited by an unfocused laser with a diameter around $100 \mu\text{m}$. Scale bar: $20 \mu\text{m}$. (b) Polarization measurements of emission from photonic crystals (black) and excitation (red). (d) PL intensity enhancement (red spheres) and emission rate inhibition (blue spheres) in perovskite photonic crystals, respectively.

The TRPL decay curves in Fig. 3.8c were fitted with three exponential functions using the following equation:

$$N(t) = N_1(0)e^{\frac{-t}{\tau_1}} + N_2(0)e^{\frac{-t}{\tau_2}} + N_3(0)e^{\frac{-t}{\tau_3}} \quad (3.5)$$

where $N(t)$ is the total number of populations from all emission channels after t time. $N_1(0)$, $N_2(0)$ and $N_3(0)$ are the initial population at $t = 0$, which represent emission lifetimes for fast and slow

channels of τ_1 , τ_2 , and τ_3 , respectively. The average emission lifetime τ_{ave} derived from key parameters in equation (3.5) is given by:

$$\tau_{ave} = \frac{\sum (A_i \times \tau_i^2)}{\sum (A_i \times \tau_i)} \quad (3.6)$$

Table 3.1 Key parameters of time resolved PL spectrum based on PhC patterned and unpatterned perovskite films (extracted from Fig. 3.8d)).

Films	$\tau_{ave}(\text{ns})$	$\tau_1(\text{ns})$	A1	$\tau_2(\text{ns})$	A2	$\tau_3(\text{ns})$	A3	A3%
a = 256 nm	7.24	1.89	0.71	5.84	0.46	18.86	0.05	4.09
a = 260 nm	20.97	2.51	0.25	8.79	0.34	25.55	0.16	21.33
a = 274 nm	9.42	1.65	0.61	5.56	0.31	17.63	0.10	9.80
a = 282 nm	15.86	2.29	0.39	7.78	0.36	21.45	0.12	13.79
unpatterned	2.66	0.86	0.65	10.3	0.37	unobserved		

Table 3.1 shows key parameters derived from fitting and the emission rate γ_{total} is calculated using the following equation:

$$\gamma_{total} = 1/\tau_{ave} \quad (3.7)$$

where τ_i and A_i are decay times and amplitudes from fitted TRPL decay curves with three exponential decay function. We observed τ_3 only from patterned photonic crystals, indicating the effect of electron on perovskite films. The perovskites are beam-sensitive materials and large electron dose can do damage and introduce defects in the perovskite films[90, 91]. As shown in Fig. 3.5b, the electron beam irradiated perovskites demonstrate lower PL intensity in comparison to unirradiated perovskites.

For comparison, we also summarized the performance of various light emitters with photonic crystals structures in Table 3.2. PL intensity enhancement and simultaneously inhibition of

emission rate are found only in several limited photonic crystals. However, perovskite photonic crystals in this work demonstrates hitherto at visible region the highest PL intensity enhancement with high inhibition of spontaneous emission rate among all light emitters with 2D photonic crystals structures.

Table 3.2 Summary of performance of light emitters with 2D photonic crystals structures

	Maximum PL Intensity Enhancement	Maximum Emission Rate Inhibition	Wavelength
Diamond PhC[92]	6	-	Red
GaInAsP PhC[69]	5	5	NIR
GaN PhC[93]	3.5	-	Blue
GaAs PhC[94]	-	70	NIR
SiO ₂ /SiN _x PhC[95]	1.5	-	Green
Silicon PhC[96]	500	-	NIR
Perovskite PhC (this work)	23.5	7.9	Green

3.3.2.6 Power Dependent PL Measurements of Perovskite Photonic Crystals

Fig. 3.9 Power dependent PL data from perovskite PhC with $a = 282$ nm. (a) PL emission spectra of perovskite PhC with $a = 282$ nm under various excitation powers at $\lambda = 355$ nm. (b) Integrated emission intensity and FWHM as function of excitation powers.

Fig. 3.9 summarizes the input-output characteristic obtained from perovskite PhC structure with $a = 282$ nm under various excitation powers at ambient environment. We observed a clear linear increase of emission intensity with the increase of pump energy density. However, the full width at half maximum (FWHM) remains almost the same without any collapse of the spectral line width. This is reasonable as the quality factor of PhC structures is not high enough to promote spontaneous emission to stimulated emission. The ladderlike behavior is related to the degradation of perovskite film under high power laser. This convinces that enhancement is solely related to the extraction efficiency improvement as we did not observe lasing when we excited with different powers.

3.4 Conclusion

In conclusion, we have successfully fabricated perovskite photonic crystals with EBL and RIE techniques and observed strong light redistribution with inhibition concurrently. Compared to unpatterned perovskite films, the light spontaneous emission rate of perovskite photonic crystals is greatly inhibited by 7.9 folds due to photonic bandgap effect, and simultaneously PL intensity is largely enhanced by a factor of 23.5 implying high extraction efficiency. Those values are still in the same order as those calculated by 3D FDTD simulations considering the errors from the fabrications and the optical constants used in the simulation (the calculated PL intensity enhancement and emission rate inhibition are 16.7 and 32.0 folds, respectively). Both experiments and simulation further prove light inhibition and energy redistribution from perovskite photonic crystals thin films. In addition, we believe our perovskite photonic crystals structures open up a new possibility for solar cell of different perovskite materials[97], as the photonic crystals can not

only brighten the devices, but also increase light absorption at bandgap region as a back side reflector[98], which in turn can improve the performance of solar cells[97].

Chapter 4 Manipulating Coherent Light-Matter Interaction with Plasmonic Nanocavities

Progress towards high performance dielectric cavities discussed above has been hindered by the diffraction limit of electromagnetic fields, which results in the difficulty of reducing the mode volume much less than the optical wavelength of interest ($V_\lambda = (\lambda/n)^3$). Strong interactions between surface plasmons in ultra-compact nanocavities and excitons in two dimensional materials have attracted wide interests for its prospective realization of polariton devices at room temperature. In this chapter, a continuous transition from weak coupling to strong coupling between excitons in MoS₂ monolayer and highly localized plasmons in ultra-compact nanoantenna is proposed. The interaction between excitons and plasmons is then directly prompted to strong coupling regime by shrinking down the thickness of spacer layer. Room temperature formation of polaritons with Rabi splitting up to 190 meV is observed with a fair polariton loss around 165 meV.

4.1 Motivation and Introduction

The strong light-matter interaction in solid state systems is a central issue in various fascinating quantum devices, including ultra-low threshold lasers[99, 100], ultra-fast workfunction switches[101], quantum information systems[102, 103] and phase transition modification[104]. The nature of this coupling depends on the formation of bosonic quasiparticles and the dispersion of hybrid states. To achieve strong light-matter interaction, it is essential to ensure that the coupling or energy exchange rate should be faster than other intrinsic dissipation rates.

In the past decades, much attention has been directed to light-matter interactions between highly confined photons (or plasmons) in nanocavities and excitons in molecules or quantum dots[19,

105]. To date, strong coupling has been demonstrated in many systems, such as organic molecules in plasmonic resonators[46], quantum dots in photonic nanocavity[19] and quantum well in Distributed Bragg Reflectors[106]. These platforms integrated with nanocavity enable strong coupling to overcome losses including cavity loss and emitter scattering[107]. However, organic molecules and quantum dots are known to suffer photobleaching and oxidization, which limit their implementation in polariton devices.

Since the discovery of graphene in 2004, the scientific community has made great effort on the exploration of graphene and other 2D materials, such as transition metal dichalcogenide (TMD), black phosphorus, hexagonal boron nitride, etc. Among them, the group-VI TMD monolayer possesses direct bandgap from the visible spectral region to near infrared. They are also shown to possess two unique features[108]: strong excitonic[109] and valley and spin dependent properties[110]. The strong excitonic effect is associated to its reduced dimension and related to the Coulomb interactions between charge carriers[109]. This feature makes TMD semiconductors promising candidates to realize light matter interactions[111] and room temperature excitonic devices operation. The second feature is associated to the electronic band structure of TMD semiconductors and this unique property have potential impacts for quantum information processing technology[112].

TMD semiconductors have gained much interests in the study of photonic devices due to their unique optical properties[113-116]. Of major interests are their high oscillator strength, large exciton binding energy and uniformity of optical properties within the entire flakes. Due to the inverse square dependence of coupling strength on mode volume $g \propto 1/\sqrt{V}$, it is important to have an optical cavity with ultra-small mode volume to achieve strong coupling[117-119]. Gap plasmon nanocavities exhibit highly localized electric field within ultra-small volume, which

enables fast and coherent energy exchanges between emitters and nanocavities. WSe₂ and WS₂ monolayers have recently exhibited Rabi splitting coupled with this type of gap plasmon nanocavities[120, 121]. However, the effect of dielectric layer thickness on the transition from weak to strong coupling has yet to be explored.

In this chapter, we demonstrate a plasmonic nanocavity based exciton polariton system with tunable coupling strength and on-demand transition between weak coupling and strong coupling. The ultra-small resonators consist of silver nanocubes over an ultra-smooth gold film (NCoM), separated by a dielectric layer. These NCoM cavities are able to confine the optical modes within an ultra-small gap, with tunable resonance frequencies and coupling strength by adjusting the nanocube size or the dielectric layer thickness. Additionally, strong coupling with Rabi splitting up to 190 meV is achieved by shrinking down the thickness of the gap between the gold mirror and nanocube. We also show that the light-matter interactions can be tuned from strong coupling to the weak coupling regime when the thickness of spacer layer is increased, which results in the observation of a 1570-fold PL intensity enhancement due to the Purcell effect. Our theoretical calculations confirm that such a transition from strong coupling to weak coupling is due to the changes of mode volume, coupling strength and electric field intensity. Based on the novel studies on the transition between weak and strong coupling, we believe this work presents an effective guideline to approach feasible designs of plasmon-exciton interaction systems.

4.2 Methods

Sample Fabrication: The NCoM plasmonic nanocavities were fabricated with bottom up self-assembly method. First, an 80-nm thick Au film was e-beam evaporated on silicon wafers with 10-nm thick titanium as adhesion film. Al₂O₃ dielectric spacer layer was then deposited using

atomic layer deposition (ALD) at 200 °C. Meanwhile, atomically thin MoS₂ flakes were grown on SiO₂/Si substrate by CVD, and were subsequently transferred onto Al₂O₃-coated gold film using Poly (methyl methacrylate) (PMMA) as mechanical protection layer during transfer. Finally, the NCoM system is formed by drop-casting a diluted silver nanocube solution (nanoComposix, 1:100) onto the prepared substrates, followed by drying with N₂ gas. The size distribution of the silver nanocubes is from 65 to 100 nm.

Optical Measurements: The scattering measurements of individual NCoMs were carried out in home-built microscope settings with xenon light source (Thorlabs) focused through 100× objective lens (NA = 0.95) in dark-field geometry. The scattered light was then collected by the same lens and directed into hyperspectral system (Cytoviva) for spectral measurement of the individual particles. The emission spectra of NCoMs were measured by a confocal Raman system (Witec) with 532 nm laser focused through 100× objective lens (NA = 0.95). The laser spot size was measured as ~ 1.5 μm. The emission was then collected by a CCD camera and a Peltier-cooled photomultiplier tube coupled to a grating spectrometer.

Numerical Simulation: Full wave simulations of NCoMs are performed to calculate plasmonic resonance using 3D FDTD Solutions (Lumerical Inc). The silver nanocubes are positioned above an 80 nm gold mirror coated with Al₂O₃ with thickness varied from 5 to 25 nm. The thickness of MoS₂ monolayer is set to 1 nm which is obtained by fitting the data from ellipsometer. The edges and corners of silver nanocubes are rounded by 3 nm and 5 nm, respectively, according to the SEM images. Moreover, the nanocubes are also coated with a 5 nm insulating polyvinylpyrrolidone (PVP) layer to prevent silver from oxidation in the air. The optical properties of gold, silver, Al₂O₃ and PVP layer are obtained from database in the software. To simulate electric field distribution, a plane wave (total field scattered field source) incidence is used to illuminate NCoM constructs

at an angle of 0° . Three monitors (frequency domain power monitors) are placed correspondingly to obtain near field electric field maps. The mode volume is obtained using “mode volume” analysis group. From this, and quality factor calculated from the lineshape at resonance, the Purcell factor is calculated as: $F_p = \frac{3}{4\pi^2} \left(\frac{\lambda_0}{n}\right)^3 \frac{Q}{V}$.

4.3 Results and Discussion

4.3.1 Optical Constants of MoS₂ Monolayer

Fig. 4.1 Real and imaginary refractive index of MoS₂ monolayer on SiO₂/Si substrate measured by a commercial ellipsometer.

Angle dependent ellipsometry measurement was carried out to measure the optical properties of the MoS₂ monolayer on Si substrate. The raw data from ellipsometry consists of amplitude ratio Ψ and phase difference Δ between the perpendicular (s-) and parallel (p-) polarization as a function of energy. After ellipsometry measurement, optical mode fitting using Tauc-Lorentz (T-L)

oscillation dispersion model was used to extract the optical constants. In this model, the energy of complex is defined as $E = \varepsilon_1 + i\varepsilon_2$, where dielectric function ε_1 and ε_2 are:

$$\varepsilon_2 = \begin{cases} \frac{AE_0C(E-E_b)^2}{(E^2-E_0^2)^2+C^2E^2} \times \frac{1}{E} & E > E_b \\ 0 & E \leq E_b \end{cases} \quad (4.1)$$

$$\varepsilon_1 = \varepsilon_1(\infty) + \frac{2}{\pi} P \int_{E_b}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi$$

in which E_0 , A , C and E_b are the position, amplitude, width and bandgap of one oscillator. And P represents Cauchy part for integration. The measurement and fitting data of the T-L mode are obtained at various incident angles. The fitting parameters are adjusted until a good fitting is achieved between model and measured spectra with the lowest mean squared error (MSE).

4.3.2 Gap Plasmonic Nanocavities

Fig. 4.2 Characterizations of gold film and Al_2O_3 coating. (a) AFM height profile of gold film. (b) AFM height profile of Al_2O_3 coated gold film. (c) Optical constants of gold film measured by ellipsometry. (d) Optical constants of Al_2O_3 coating measured by ellipsometry.

Benefiting from electron beam evaporation and atomic layer deposition, both gold film and Al_2O_3 coating demonstrate ultrasmooth surface with roughness of 0.123 nm and 0.135 nm (Fig. 4.2), respectively. The measured optical constants of gold film is quite consistent with literature[122]. The real refractive index of 5 nm Al_2O_3 coating on gold film is nearly constant over the range of 600 nm to 1700 nm while no extinction is observed due to its thin thickness.

The NCoM systems consist of a silver nanocube positioned on the top of Al_2O_3 coated gold film, as shown in Fig. 4.3a. The plasmon resonance frequencies of NCoMs can be easily tuned from red to green either by adjusting the thickness of spacer layer or the size of nanocube (Fig. 4.3b and c). For example, when the size of nanocube increases from 65 nm to 100 nm, wide range of resonance

from 620 nm to 720 nm is tracked in Fig. 4.4, which shifts across the A exciton in MoS₂ monolayer. The fundamental plasmonic mode of NCoM is localized in the gap with the dominant electric field oriented in the vertical direction, transverse to the gap. And the spontaneous emission rate of a dipole is given by:

$$\gamma_{\text{sp}}(\vec{r}) = \frac{\pi\omega}{3\hbar\epsilon_0} |\vec{p}| \rho(\vec{r}, \omega) + \gamma_{\text{int}}^0 \quad (4.2)$$

where $\vec{p}$ is the dipole moment, $\vec{r}$ is the position of dipole and γ_{int}^0 is the internal non-radiative decay of the emitter. $\rho(\vec{r}, \omega)$ is the local density of states, and it can be greatly modified in plasmonic environment:

$$\rho(\vec{r}, \omega) = \frac{2\omega}{\pi c^2} \text{Im}(\vec{u} \cdot \vec{G}(\vec{r}, \vec{r}, \omega) \cdot \vec{u}) \quad (4.3)$$

where $\vec{u}$ is the orientation of the dipole and $\vec{G}(\vec{r}, \vec{r}, \omega)$ is the Green function which describe the interaction between the plasmonic environment with dipole. When the gap separation increases, this interaction becomes weaker as the electric field gets weaker, thus, the emission rate enhancement decreases, as shown in Fig. 4.3d and e. In addition, the interaction is also determined by the orientation of dipole, and the vertical oriented has higher enhancement compared with horizontal dipole as vertical dipole can be coupled with fundamental plasmonic modes. Smaller gap with stronger field confinement is required to trigger the strong coupling if the exciton is in-plane.

Fig. 4.3 Tunability of plasmonic cavity resonance in NCoM systems. (a) Schematic of NCoM. Tuning cavity resonance (b) by varying nanocube sizes on a fixed spacer thickness (5 nm) and (c) by varying spacer thickness with fixed nanocube size (edge length: 80 nm). (d) and (e) Spontaneous emission rate of an emitter at $\lambda = 667$ nm with different dipole orientation.

Fig. 4.4 Simulated scattering spectra of 5 nm spacer NCoM nanocavities with various silver nanocube sizes. The insets are the corresponding SEM images of silver nanocubes.

4.3.3 Coupling MoS₂ monolayer with NCoMs

The MoS₂ was grown on SiO₂/Si substrates by chemical vapor deposition (CVD) methods and then transferred onto an ultra-smooth gold film (see Methods). The monolayer characteristic of MoS₂ was confirmed by AFM and the thickness was determined as ~ 0.77 nm (Fig. 4.5a). Typical bright and dark field images of hybrid nanostructures are shown in Fig. 4.5, with MoS₂ monolayer in triangular shapes and silver nanocubes in black dots in bright field image (Fig. 4.5a) or colorful points in dark field image (Fig. 4.5b). The gap plasmon nanocavity systems consist of self-assembled silver nanocubes on a gold mirror with CVD grown MoS₂ monolayer and a thin Al₂O₃ spacer layer embedded into the gap (Fig. 4.5c). Briefly, MoS₂ monolayer is transferred onto Al₂O₃-coated ultra-smooth gold film, followed by drop-casting silver nanocubes to form NCoM systems (Fig. 4.5c) (see Methods). In these plasmonic gap nanocavities, the ultra-small mode volume can

yield high optical field confinement which is sufficient to produce both weak coupling and strong coupling[123].

Fig. 4.5 Construction of MoS₂-NCoM hybrid. (a) Bright field of optical image of monolayer MoS₂ flake. The inset shows AFM height profile of MoS₂ monolayer on Al₂O₃ coated gold film. (b) Dark field scattering image of MoS₂ monolayer corresponding to panel a. Scale bar in a and b is 20 μm. (c) Three-dimensional illustration of a NCoM cavity encapsulating monolayer MoS₂ flakes. Insets show a transmission electron microscopy (TEM) image of an individual silver nanocube (scale bar: 20nm) and cross-sectional schematic of a NCoM construct.

4.3.4 Strong Coupling Regime in MoS₂-NCoM Constructs

Fig. 4.6 Signature of strong coupling in NCoM constructs with 5 nm spacer layer. (a) Power dependent PL emission of MoS₂ on gold film (dashed lines) and incorporated into NCoM systems (shadow plots). (b) Dark field spectra (black) and bright field PL emission (blue) from same NCoM construct. The shadow plot shows the PL spectra from MoS₂ monolayer on gold film. (c) Normalized dark field scattering spectra from different individual NCoMs. Insets are the corresponding scattering images. (d) High energy polariton (HEP) and low energy polariton (LEP) as a function of detuning. (e) The contributions of exciton and plasmon to HEP and LEP against detuning.

MoS₂ monolayer is chosen in our study for its large exciton binding energy (≥ 570 meV)[124] which results in a stable PL emission (Fig. 4.6a) and allows room temperature strong coupling operation. Typically, there are two excitons named A and B, associated with the splitting of valence band in first Brillouin zone[125]. Usually, only A exciton is manifested as dominant peak in PL spectra due to the low intrinsic quantum efficiency of B exciton[126]. When MoS₂ monolayer is incorporated into NCoM with 5 nm spacer on resonance, the strong coupling between excitons and plasmons is observed in PL spectra at bright field (Fig. 4.6a). Instead of single A exciton peak on

gold film or glass, two split peaks are observed in PL spectra with high energy polariton (HEP) branch at 630 nm and low energy polariton (LEP) branch at 681 nm. Compared to dark field spectra from the same NCoM construct, the splitting energy in PL is smaller than that of dark scattering spectra (Fig. 4.6b). The much smaller splitting energy in PL is attributed to the faster polariton relaxation rate than emission rate and also the difference in splitting between absorption and scattering[127]. Similar to typical strong coupling systems, the HEP emission is much weaker than that of the LEP, which is due to the fast nonradiative rate with low quantum efficiency and the relaxation toward uncoupled excitonic states in HEP branch[106, 127]. Dark field measurements are conducted on many individual NCoM systems with 5 nm Al₂O₃ spacer layer in Fig. 4.6c. Tuning plasmon resonance by varying nanocube size results in two split peaks with different spectral contrasts and a characteristic dip at the wavelength of A exciton, indicating the occurrence of strong coupling. The positions of measured nanocubes are determined with dark field measurement and the same region is then imaged with SEM to characterize the corresponding silver nanocube sizes.

To describe this plasmon-exciton interaction process, the classical coupled harmonic oscillator model (CHOM) is used to provide an accurate physical analyzer. In this model, the involved excitons are viewed as a “super oscillator”, and then the whole process is pictured as two coupled oscillators[19]:

$$\begin{pmatrix} E_{SP} - i\Gamma_{SP}/2 & g \\ g & E_{ex} - i\Gamma_{ex}/2 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E_{\pm} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (4.4)$$

Here E_{SP} and E_{ex} are the energies of NCoM plasmon and A exciton in MoS₂ monolayer, respectively; g is the coupling strength of the hybrid system; Γ_{SP} and Γ_{ex} represent the line widths of plasmon and A exciton; α and β are the eigen coefficients that satisfy $|\alpha|^2 + |\beta|^2 = 1$; and $E_{\pm}$

are the eigen values associated with the energies of the hybrid nanostructure. Given that the widths of plasmon and exciton are small compared to their energies, the energy of the hybrid systems can be estimated as:

$$E_{\pm} = \frac{1}{2}(E_{ex} + E_{SP}) \pm \sqrt{g^2 + \frac{1}{4}(\delta - \frac{i}{2}(\Gamma_{SP} - \Gamma_{ex}))^2} \quad (4.5)$$

in which $\delta = E_{SP} - E_{ex}$ is the detuning energy between plasmon and A exciton in MoS₂ monolayer.

The Rabi Splitting Ω can be calculated at $\delta = E_{SP} - E_{ex} = 0$:

$$\Omega = E_{+} - E_{-} = \sqrt{4g^2 - \frac{1}{4}(\Gamma_{SP} - \Gamma_{ex})^2} \quad (4.6)$$

The line widths of plasmon and A exciton are extracted to be 280 meV and 50 meV, which are extracted from the scattering spectrum of nanocavity and the PL spectrum of monolayer, respectively. Fig. 4.6d shows dispersion curve extracted from the dark field scattering spectra in Fig. 4.6c, together with a fitting from the CHOM model. The results show a clear anti-crossing behavior with a Rabi splitting $\Omega = 190$ meV at $E_{SP} = E_{ex}$, which satisfies strong coupling criterion ($\Omega > \frac{\Gamma_{SP} + \Gamma_{ex}}{2}$)[128]. The polariton system can be characterized by the comparison of

Rabi splitting with polariton loss. People already demonstrated strong coupling using low loss plasmonic structures with narrow resonance width[129-133]. However, this splitting energy is hitherto the largest Rabi energy splitting among all plasmon-exciton polariton systems with TMD 2D materials. We also note that the average loss of polariton of 165 meV in our observation is still comparable with that in strong coupling observed in WSe₂ and WS₂, and better than 100-meV losses that were observed very recently in both mentioned materials[130, 133] (see Table 4.1). The contributions of plasmon and exciton components to the HEP and LEP can also be calculated from

fitting (Fig. 4.6e). The plasmon (exciton) constituent gradually dominates HEP (LEP) when the detuning changes from negative to positive. Notably, strong coupling has been demonstrated by coupling MoS₂ with Fano resonators[106, 134]. However, owing to the low confinement of optical mode in these nanocavities, the strong coupling can only be clearly observed at cryogenic temperature (77 K) with a small Rabi splitting of 58 meV. Also, a big challenge for Fano resonators lies in the difficulty of resonance tunability. On the other hand, a spectra splitting was also observed in MoS₂/Ag nanoparticles hybrid structures[135]. However, only PL enhancement at weak coupling regime was observed without anti-crossing behavior.

Table 4.1 Literature overview of strong coupling in 2D materials. DBR: distributed Bragg reflector, FP: Fabry–Pérot cavity.

Source	Strong coupling operation temperature	2D Materials	Cavities	Wavelength (nm)	Splitting Energy (meV)	$\Omega / \Gamma_{Polariton}$ ($\Gamma_{Polariton} = \frac{\Gamma_{SP} + \Gamma_{ex}}{2}$)
This work	RT	MoS ₂ monolayer	NCoM	667	190	1.15
[136]	✓	WSe ₂ multilayer	NPoM (Au nanosphere on Au film)	761	135	1.44
[137]	✓	WS ₂ monolayer	NCoM	615	145	1.07
[138]	✓	MoS ₂ monolayer	DBR	662	46	
[139]	77K	MoS ₂ monolayer	Ag nanodisk arrays	630	58	
[121]	✓	WSe ₂ monolayer	NCoM	750	36.7	0.42
[140]	✓	WS ₂ monolayer	DBR	597	36	2.06
[141]	✓	WSe ₂ monolayer	DBR	755	23.5	
[142]	✓	WSe ₂ monolayer/multilayers	Gold Bi-pyramids	743~756	103 meV	1.19
[143]	✓	WS ₂ monolayer	FP	620	101	2.35
[133]	✓	WS ₂ multilayers	Ag nanoparticle	642	100	1.57
[144]	✓	WS ₂ monolayer/multilayers	Au nanodisk	632	175	1.64

4.3.5 Weak Coupling Regime in MoS₂-NCoM Constructs

Fig. 4.7 Photoluminescence enhancement from NCoM constructs at weak coupling regime. (a) PL spectra from MoS₂ monolayer at different environments. (b) Experimental photoluminescence enhancement factor (upper, with red dashed line to show the guidance) and calculated normalized Purcell factor (lower, normalized to values with 10 nm spacer) as a function of spacer thickness in NCoMs. (c) Electric field intensity distribution within the nanocube and MoS₂ monolayer at $\lambda=665\text{nm}$. The position of nanocube is marked with dashed square. Scale bar = 50 nm.

By further increasing the spacer thickness to 10 nm and more, only PL enhancement can be observed instead of Rabi splitting. To quantitatively investigate the enhancement performance of NCoMs constructs, a series of experiments were conducted on (i) samples of MoS₂ monolayer coupled into NCoMs (ii) samples with MoS₂ monolayer transferred on a glass slide without any nanocube. Samples were excited by a 532 nm continuous wave laser and the PL signal was collected by a spectrometer equipped with a photomultiplier tube (PMT) (see Methods). The

isolated silver nanocube in NCoMs was marked out from dark field images and subsequently PL measurements were carried out. Three orders of magnitude are observed in PL spectra (Fig. 4.7a). Given that the area of PL collection is much larger than that of nanocube which contributes to the PL intensity enhancement, the average enhancement of NCoMs is then quantified by the PL enhancement factor (EF)[145]:

$$EF = \frac{I_{NCoM}}{I_{glass}} \times \frac{A_{spot}}{A_{NC}} \quad (4.7)$$

where I_{NCoM} (I_{glass}) is the PL intensity from MoS₂ monolayer coupled in an individual NCoM (on glass), A_{spot} and A_{NCoM} are the area of laser spot (diameter $\sim 1.5 \mu\text{m}$) and that of an individual silver nanocube, respectively (Fig. 4.7b inset). The calculated EF from equation (4.7) is plotted against the thickness of spacer layer in Fig. 4.7b. When the spacer thickness increases from 10 nm to 25 nm, a dramatic decrease in EF is observed from 803 to 225 (Fig. 4.7b). Such a decrease in EF is accompanied by a simultaneous decrease in the Purcell factor (Fp).

The Purcell factor is defined as:

$$F_p = (\gamma_r + \gamma_{nr}) / \gamma^0 \quad (4.8)$$

And enhancement factor of PL intensity from experiment is calculated as:

$$EF = \left[\gamma_r / (\gamma_r + \gamma_{nr}) \right] / \left[\gamma_r^0 / (\gamma_r^0 + \gamma_{nr}^0) \right] \quad (4.9)$$

Here, γ_r and γ_{nr} are radiative rate and nonradiative rate in NCoM construct while γ_r^0 and γ_{nr}^0 are radiative rate and nonradiative from pristine MoS₂ monolayer. The thickness of gap is larger than 10 nm, the nonradiative recombination (including quenching and absorption) can be assumed as a

constant[146]. Then considering $\gamma_r \ll \gamma_{nr}, \gamma_r^0 \ll \gamma_{nr}^0$ and $\gamma_{nr} \approx C\gamma_{nr}^0$ (C is a constant), equation (4.9) can be simplified as:

$$EF = \gamma_r / C\gamma_r^0 \quad (4.10)$$

Combining equation (4.8) and (4.10), we can get:

$$F_p = CEF + \gamma_{nr} / \gamma_r^0 \approx C(EF + \gamma_{nr}^0 / \gamma_r^0) \quad (4.11)$$

The calculated F_p (normalized to the value from the spacer with 10 nm thickness) exhibits a similar trend to that of EF, indicating that the reduction of EF is attributed to the decline of F_p . The enhanced PL and F_p are in good agreement with the faster lifetime in NCoM compared to that on glass. Although the detuning range of NCoM cavity is large enough reach the energy of B exciton, there is no effect of cavity on B exciton in the spectra. This is attributed to the low quantum efficiency and very high nonradiative loss in B exciton in our MoS₂ samples, which are different with other work[147].

We further investigated the electric field intensity distributions in NCoMs (Fig. 4.7c). We find that the in-plane optical mode is enhanced in the gap at the four corners of the silver nanocube. The energy density is mostly distributed in MoS₂ monolayer rather than in nanocube due to the large refractive index of MoS₂ monolayer, indicative of higher local density of states (LDOS).

4.3.6 Analyses of Transition between Strong Coupling and Weak Coupling

Fig. 4.8 Comparison of calculated mode volume, coupling strength and electromagnetic field in NCoMs with different spacer thickness. (a) Optical mode volume (red) and coupling strength (blue) vs. the thickness of spacer in NCoM constructs. Strong coupling regime is shaded in yellow. The dashed lines give eye guidance. (b) Measured and simulated scattering spectrum of a single NCoM without MoS₂, in normalized units. (c) Electric field enhancement as a function of gap thickness. Insets are electric field mapping of three different NCoM. Noting that the size of nanocube is adjusted to overlap A exciton in MoS₂ monolayer. Scale bar: 50 nm.

In order to further understand this transition between strong coupling and weak coupling, we calculated the mode volume, coupling strength and electric field intensity in NCoMs with different spacer thicknesses. The coupling strength g is an essential criterion to characterize the strong coupling and can be extracted from equation (4.4)[105]. Based on the usual definition, g can also be estimated as[105]:

$$g = \mu_m \sqrt{\frac{4\pi\hbar Nc}{\lambda \epsilon \epsilon_0 V}} \quad (4.12)$$

where μ_m is exciton transition dipole moment, N is the exciton number, λ is the wavelength, V is the mode volume, ϵ is the dielectric permittivity and c is the speed of light. N can be estimated from the exciton areal density in MoS₂, σ_{exc} and the mode effective area, A . From equation (4.12), a large coupling strength can be achieved by reducing the mode volume and optimizing the number

of excitons involved in the interaction through the effective area in the emitter. The mode volume can be obtained by the integration of energy density over the volume of NCoM, and normalized to its maximum value, which is still located at the vicinity of the emitter position[46, 148, 149]:

$$V(\omega) = \frac{\int W(\vec{r}, \omega) d^3 \vec{r}}{\max \left[W(\vec{r}, \omega) \right]} \quad (4.13)$$

where $W(\vec{r}, \omega)$ is complex energy density inside the metal and is given by:

$$W(\vec{r}, \omega) = \frac{1}{2} \left(\frac{\partial [\omega \varepsilon(\vec{r}, \omega)]}{\partial \omega} \varepsilon_0 |E(\vec{r}, \omega)|^2 + \mu_0 |H(\vec{r}, \omega)|^2 \right) \quad (4.14)$$

where $\varepsilon(\vec{r}, \omega)$ is the material permittivity at position $\vec{r}$. In this calculation, a normal incident plane wave is used to illuminate the NCoM and the scattered electric field is collected to represent the plasmonic mode from NCoM. With the thickness of spacer in NCoM decreasing gradually, the mode volume shrinks dramatically owing to the high confinement of plasmon modes while the extracted g increases tremendously (Fig. 4.8a) and strong coupling regime occurs when the thickness is smaller than ~ 7 nm. The extracted g in this plot also depends on the number of the excitons through the relationship between the effective mode area and the spacer thickness. We calculated the electric field intensity in different NCoMs, noting that the nanocube size is adjusted to tune the plasmon resonance of NCoM overlapping with A exciton in MoS₂ monolayer (Fig.4.8b). We find that the electric field intensity decreases exponentially with the increase of spacer thickness (Fig. 4.8c). Although smaller spacer thickness will enable larger coupling strength, it is faced with the difficulty in the fabrication of homogeneous spacer layer. Based on the reasoning above, embedding MoS₂ monolayer into NCoM cavities with thick spacer can trigger weak

coupling with high PL enhancement. Shrinking down the spacer layer to decrease mode volume and prompt field confinement can increase the coupling strength, thus switching on light-matter interactions at strong coupling regime.

4.4 Conclusion

The significant role of spacer thickness on strong coupling and weak coupling from MoS₂ monolayer in NCoM has been explored experimentally and theoretically. We successfully demonstrated the transition from weak coupling regime with 1570-fold PL intensity enhancement to strong coupling regime with Rabi splitting as large as 190 meV, which to the best of our knowledge marks the largest plasmon-exciton Rabi splitting among all TMD at room temperature. The formation of polariton states in NCoM is attributed to the collaborative effect of large exciton binding energy in MoS₂ monolayer, ultra-small mode volume and ultra-strong optical mode confinement in NCoM. Both the experimental and theoretical studies performed here provide a new guideline for selecting suitable plasmonic nanostructures to implement strong coupling operation.

Chapter 5 Engineering Single Photon Sources in hBN Monolayers

Efficient generation and extraction of single photon from solid state quantum emitters is a vital requirement for future quantum techniques. Plasmonic nanostructures, demonstrated in previous chapter, hold the capacity of strong modification of photonic environment. To approach the limit of light-matter interaction between single quantum emitters and plasmonic nanocavities, we first engineer single photon sources in hBN monolayers. hBN has emerged as a promising 2D material for photonics device due to its large bandgap and flexibility in nanophotonic circuits. In this chapter, we report bright and localized luminescent centers can be engineered in hBN monolayers and flakes using laser irradiation. Remarkably, the color centers in hBN flakes exhibit room temperature cleaner single photon emissions with $g^2(0)$ ranging from 0.20 to 0.42, a narrower line width of 1.4 nm and higher brightness compared with monolayers. Our results pave the way to the engineering the deterministic defects in hBN formed by laser pulse and show great prospect for application of defects in hBN used as nano-size light source in photonics.

5.1 Motivation and Introduction

Unique optical properties of 2D semiconductors such as graphene, transition metal dichalcogenides (TMDCs), and boron nitride have attracted considerable attention[150-156]. Among all potential electronics device, photoelectrical properties of 2D hexagonal boron nitride (hBN) are of great important due to its wide bandgap[151, 157-159], graphene-like structure[154, 160-163], high thermal conductivity[164, 165] and chemical stability[166, 167]. From this perspective, fluorescent properties of hBN monolayers have been explored since ultra violet emission in hBN monolayers was reported[168]. Particularly, engineering the luminescent centers in hBN is an aspiring goal because the centers are excellent room temperature single photon

emitters[169, 170]. To this extent, localized and patterned defects are strongly preferred to form sub bandgap excitation sources in hBN monolayers while preventing excitonic combination[157]. Defects engineering in hBN can be achieved mainly by annealing[169, 170], electron[169, 170] or ion beam[171] irradiation, and wrinkle process[172]. The defects origins could be predicted as three stable native point defects in hBN monolayers defined as a boron vacancy (V_B), a nitride vacancy(V_N) and N_BV_N in which one nitrogen atom is missing and the boron site is occupied by nitrogen[173, 174]. Toan Trong Tran et. al. created atomic point defects in hBN monolayers using annealing and electron beam, finding that the photoluminescence (PL) peak around 623 nm was closely related with N_BV_N point defect and attributed to the zero phonon line (ZPL) with single photon characteristics[169, 170]. However, the color centers created by annealing, electron beam and wrinkling in hBN monolayers are uncontrollable and distributed randomly.

Although the electron beam irradiation with high voltage generates smaller beam focus than that of laser irradiation, laser irradiation can be conducted at ambient environment with no vacuum requirement, which is simpler and more flexible. Laser irradiation is now widely used owing to its flexibility to control the energy and position. Laser irradiation was previously utilized to fabricate nanostructures[175-178], graphene oxide deposition[179, 180] and synthesis of nanowires[181-183]. Laser irradiation is also used to create color centers in cBN crystal[184] and diamond[185], although the emission is very weak with broad peaks. As it can be seen, it is easier to find color centers employing laser irradiation. In this chapter, with laser irradiation technology, we successfully engineered color centers in hBN monolayers and hBN flakes. Interestingly, hBN-to-cBN transition emerges around the laser irradiation region in hBN monolayers, which was not reported from voids created by laser irradiation in single crystal of cubic boron nitride (cBN)[184]. The strong and sharp emission of addressed color centers is mainly found surrounding voids. Fine

emissions with a full width at half-maximum (FWHM) of 4.5 nm and 1.4 nm are found in laser irradiated hBN monolayers domains and flakes, respectively, of which both are much narrower than that of ~ 10 nm from defect emission created by electron beam irradiation[170]. Color centers in hBN flakes are much brighter than that in hBN monolayers and poor single photon emitters are found in irradiated hBN monolayers while bright narrowband single photon emissions with $g^2(0)$ as low as 0.20 are detected in hBN flakes. Additionally, there is hitherto no report on the quantum properties from localized defects in hBN monolayers and flakes created by laser irradiation. Our results not only reveal optical properties of color centers in laser irradiated hBN, but also provide a new approach to engineering controllable defects in hBN.

5.2 Methods

Sample fabrication: 2D hBN monolayers were obtained using CVD method as reported previously[186]. With the ammonia borane (Sigma-Aldrich) heated at 85 °C and the amount controlled at around 10 mg, the hBN monolayers were grown on copper at a fixed temperature of 1050 °C for 0.5 h after annealing the copper. The growth was done under Ar (200 sccm) protection with a small amount of H₂ (18 sccm). After growth, the hBN was transferred onto SiO₂/Si substrate using electrochemical delamination[187]. Finally, the sample was annealed in tube furnace at 850 °C for 0.5 h with argon flow and then cooled to room temperature. hBN flakes were prepared by directly drop casting 50 μ L commercial BN pristine flakes solution (Graphene Supermarket) onto SiO₂/Si substrate and dried at room temperature.

Laser irradiation setup: Laser pulse (Chameleon Ultra Laser System) of $\tau_p = 140 \pm 20$ fs duration was focused on the surface of hBN monolayers with a lens of numerical aperture NA= 0.65

(Olympus 40×). The laser irradiation was performed at fundamental $\lambda=700$ nm with repetition rate of 80 MHz for 1 s in Fig. 5.1~ 3 and 0.5 s for Fig. 5.4, Fig. 5.5 and Fig. 5.6.

Surface characterization: LEO 1550 Gemini was used to take scanning electron microscope (SEM) images. Atomic force microscope (AFM) setup equipped with Cypher scanning probe microscope and Asylum Research MFP-3D was used with tapping mode to characterize the morphology of samples.

Raman measurement: Raman spectra was conducted using 532 nm 37 μ W continuous wave laser (WITec focus innovations) with microscope objective numerical aperture NA=0.8 (Olympus 100x). The Raman was operated at the diffraction limit with a laser spot size of less than 1 μ m. The PL mapping was performed using Raman set up with the same excitation laser and objective. The scanning step of Raman and PL intensity mapping is 0.2 ~ 1 μ m/step.

Photon antibunching measurements and data fitting: Photon antibunching was performed using the HBT (Hanbury Brown and Twiss) setup with continuous wave laser at 532 nm at 40 μ W and two photon counting detector modules (PDM) from Micro Photon Devices connected to single photon counting acquisition module (PicoHarp 300). We filtered emission with linear variable filters (Ocean Optics LVF-HL) and fluorescence bandpass filter at 630 ± 38 nm from Semrock (FF01-630/38-25). The results in Fig. 5.4d were fitted with the following standard expressions[188]:

$$g^{(2)}(\tau) = 1 - (1 - g^{(2)}(0))e^{(-|\tau|/\tau_{tot})} \quad (5.1)$$

where τ_{tot} is interlevel rate constant related to the lifetime of combination and pumping, and defined as:

$$\frac{1}{\tau_{tot}} = \frac{1}{\tau_{rec}} + \frac{1}{\tau_{pump}} \quad (5.2)$$

where τ_{rec} and τ_{pump} are the lifetimes of photon recombination and pumping, respectively. In this paper, we use low power laser excitation (40 μ W), thus τ_{pump} can be considered as infinite compared with τ_{rec} and then:

$$\tau_{tot} \approx \tau_{rec} \quad (5.3)$$

The defect can be confirmed to be single photon emitter once $g^{(2)}(0) < 0.5$ [189]. The long time scale second order autocorrelation data was fitted using three-level model[190]:

$$g^{(2)}(\tau) = a + be^{-\tau/\tau_2} + ce^{-\tau/\tau_3} \quad (5.4)$$

where a, b and c are constants while τ_2 and τ_3 are related to the interlevel rate constants.

PL measurements: Microphotoluminescence measurements were performed using free space excitation and collection through visible–near infrared microscope objective (Olympus 80 $\times$, NA = 0.90)[191]. The samples were excited with a ps-pulsed laser diode emitting at 371 ± 5 nm wavelength with 10 MHz repetition rate, focused to a beam size of 2 μ m. Luminescence was detected using a Peltier-cooled photomultiplier tube (Hamamatsu H7422 series) coupled to a grating spectrometer (Edinburgh Instruments F900 and Bentham TMS300). Time-resolved decay traces were acquired by a time-correlated single-photon counting acquisition module (Edinburgh Instruments, TCC900) at selected wavelength of 626 ± 5 nm. The PL images were recorded using charge coupled device (CCD) camera with a band pass filter of 625 ± 20 nm.

5.3 Results and Discussion

5.3.1 Raman Characterization of Laser Irradiated hBN Monolayer

Fig. 5.1 Raman spectra of laser irradiated hBN monolayers. (a-b) The corresponding Raman spectrum of the points marked in (c). (c) The microscopy image of laser irradiated hBN monolayers. Scale bar: 5 μm .

The hBN monolayers were synthesized using chemical vapor deposition (CVD) method and then transferred to SiO₂/Si substrate, see Methods. Before hBN monolayers were irradiated, the as-grown hBN monolayers were characterized with Raman and atomic force microscope (AFM). The Raman exhibits a peak of 1370 cm⁻¹ and the thickness of monolayers from AFM characterization is ~ 2.8 nm. Both features are the signatures for pristine hBN monolayers. Then, we created defects in these monolayers by laser irradiation under ambient environment, see Methods.

Before we characterized emission properties of the defects, we needed to confirm the presence of hBN monolayers around the void. When applying high energy to hBN, there could be a chance for phase transition[192, 193]. To verify this, Raman measurement was carried out around the irradiated void. Fig. 5.1a shows the Raman spectra of points along the line in Fig. 5.1c which is passing through the void with a diameter around 1.5 μm . The Raman peaks around 1,460 and 1,370 cm⁻¹ indicating the substrate of silicon and hBN respectively[194, 195]. The center of void shows

no peak of $1,370\text{ cm}^{-1}$ as no hBN monolayers are left after the laser irradiation. The Raman spectrum of crystal cBN can be characterized with two isolated transverses optical (TO) mode at 1056 cm^{-1} and longitudinal optical (LO) vibrational mode at 1305 cm^{-1} [196]. However, the changes of TO and LO occur as a function of cBN crystal size[197]. In nano-crystal cBN, TO mode disappeared while the LO mode was short shifted and got broadened. These previous results are well related with the data here, indicating the obvious peak of 1295 cm^{-1} at L2 and L5 in Fig. 5.1a is due to the presence of nano-crystal cBN. The small G band around 1600 cm^{-1} at L2 and L5 comes from the carbon contamination which may be induced from hydrocarbon during laser processing or the residual of polymethyl-methacrylate (PMMA) during transfer. Due to low intensity of G band, the content of carbon is extremely low that can be ignored in the following discussion. On the other hand, the Raman spectra of points along the curve is almost the same in Fig. 5.1b, indicating the phase components in transition region are homogeneous hBN to cBN transition. This structural transformation is attributed to the high energy of laser irradiation and the spectra is similar to that of transformation from hBN to cBN due to the applied He^+ ion implantation[171].

5.3.2 PL and TRPL from Laser Irradiated hBN Monolayer

Transient PL spectra of the laser irradiation region was recorded over a large area using confocal microscopy with a $371 \pm 5\text{ nm}$ laser excitation. The main narrow PL peak at 624 nm is fitted with Gauss in Fig. 5.2a, and this wavelength with FWHM of 10.6 nm matches very well with 623 nm emission from $\text{N}_\text{B}\text{V}_\text{N}$ point defects[169] whereas the broad sub peak around 640 nm is similar with the PL emission from cBN color centers[198].

The optical radiative transition lifetime was carried out using time resolved fluorescence measurements over a large scale up to 500 ns (Fig. 5.2b). The signals were fitted by a single exponential function with 4 ns and 166 ns for short decay and long decay, respectively.

To further study the type of emission center, emission polarization test was conducted as shown in Fig. 5.2c to gain further insights into the relationship between polarization of excitation and emission. Fitted by $\cos^2(\theta)$ function, the results indicate that the emission at 624 nm is linearly polarized with dipole characteristics[199] and the polarization is coinciding with that of excitation. Thus, the polarization of emission can be easily controlled by excitation.

Fig. 5.2 Emission properties of laser irradiation region in hBN monolayers. (a) Room temperature PL spectra of laser irradiated region with Gauss multi peaks fitting. (b) Time resolved photoluminescence decay curve fitted with exponential function (white). (c) The polarization of PL intensity from experiment (black balls) and fitting (red line). The vertical arrow line shows the polarization of excitation laser.

Fig. 5.3a and b exhibit the PL intensity mapping at 624 nm at different regions marked in Fig. 5.3c and the mapping was conducted with a step of 1 μm . One circular area in the center with much lower PL intensity in contrast to the transition region can be clearly observed in Fig. 5.3b. And the pristine region is also as dark as central circular area (Fig. 5.3a, b), which means there are much less color centers at pristine regions compared with transition region. The highest PL intensity is up to 1,930 counts/s at transition region which consists of hBN and cBN according to Raman spectra Fig. 5.1. The PL mappings further prove that the enhanced sharp emission in PL spectra in

Fig. 5.2a comes from the color centers in hBN and cBN transition region. These results illustrate that the bright color centers are created by laser irradiation not by thermal annealing.

Fig. 5.3 PL mappings around laser irradiation region for monolayers. (a-b) PL intensity mapping of blue square (a) and red square (b) in microscope (c); (c) Corresponding optical microscope image of laser irradiated hBN monolayers. The scale bar in the micrographs is 10 μm . The void is created by laser at 1.93 W.

5.3.3 Antibunching from Laser Irradiated hBN Monolayer

To gain further insights to the characters of defects, single atomic defect is preferred for the characterization and it is easier to get separate single atomic defect at small monolayers domains.

To this extent, we performed PL intensity mapping measurement with high resolution of 0.2 μm /step at another irradiated region. Unlike the region in Fig. 5.3, the hBN monolayers in this experiment comprise of small monolayers domains and its presence can be identified by Raman mapping. Fig. 5.4b shows bright luminescent spot with 2,100 counts/s in scanning confocal PL mapping of hBN monolayers around the irradiated region as marked in Fig. 5.4a and this may correspond to the emission from single defects. The area of PL and Raman peak spot is about $0.5 \times 0.5 \mu\text{m}^2$, which is more or less the same size as the diffraction limit of the confocal setup. Unlike Fig. 5.2, we performed experiments in another defects with longer excitation wavelength of 532 nm and we expect the emission properties in Fig. 5.4 may differ from those in Fig. 5.2[170, 200].

To verify this assumption, PL spectra and autocorrelation functions over long time scales were conducted, which can offer information on metastable states with long time decay[201, 202]. Fig. 5.4c taken from the bright spot in Fig. 5.4b shows the narrow emission at 628 nm with FWHM of 4.1 nm, which is much better than that of 10.6 nm in Fig. 5.2 and the previous electron-beam irradiated hBN monolayers[170]. The slight shift of emission wavelength between Fig. 5.2a and Fig. 5.4c is related with the diversity between different setups, which is still in the accuracy of the setup. To identify single photon sources, Hanbury-Brown-Twiss (HBT) interferometry antibunching experiments were carried out to record second order autocorrelation functions. Fig. 5.4d illustrates $g^{(2)}(\tau)$ curve for the emission of 628 nm at room temperature, indicating photons antibunching with $g^{(2)}(0) \sim 0.50$ with poor single photon emitter and a lifetime τ_{tot} of 3.7 ns, consistent with the lifetime value measured by time resolved photoluminescence decay at irradiated large monolayers. Longer time scale second order autocorrelation function is shown in Fig. 5.4e. Fitted with multiexponential (see methods) function, we obtained additional decay times: $\tau_2 = 374$ ns and $\tau_3 = 1.7$ μ s.

Fig. 5.4 Antibunching of nanosized point defect in hBN. (a) Optical micrograph. The scale bar in the mapping and the micrograph is 1 μm . (b, top) PL intensity mapping of dash rectangular area in (a). (Bottom) The PL intensity profile of laser irradiated hBN, measured along the dashed white line cut in the top panel. (c) PL spectra with Gauss fitting (red solid line) taken from the bright spot in (b). (d) Normalized second-order correlation functions showing that $g^2(0) \sim 0.50$. (e) Second-order autocorrelation function recorded over a longer time scale. The second order autocorrelation was fitted with exponential function (black solid line). Scale bar: 2 μm . The void is created by laser at 1.93 W.

5.3.3 Single Photon Emission in Laser Irradiated hBN Flakes

Compared with large monolayers, the hBN monolayers domains intend to show narrower emissions after laser irradiation. Thus, we arise an assumption that the optical properties are closely related to size of hBN and hBN flakes with smaller size of ~ 200 nm should exhibit better optical properties. To verify this, we performed laser irradiation onto hBN monolayers and flakes with different laser powers. Fig. 5.5 shows optical properties of hBN monolayers and flakes after femtosecond laser processing. Bright fluorescence was clearly observed at irradiated regions, indicating the formation of optically active defects or color centers. The defects in hBN monolayers have almost the same wavelength of emission with that in flakes, suggesting the same type of defects are induced by laser (Fig. 5.5a and f). More importantly, we found narrow emissions

(1.4 nm width) in hBN flakes without damaging substrate after low laser power processing. This narrower linewidth compared with that of monolayer results from its higher uniformity of defects than monolayer. However, fluorescence was no longer observed from hBN monolayers after laser processing without damaging substrate, suggesting the absence of defects. This is due to hBN monolayers have a wide bandgap (~ 6 eV) and the thickness (2.8 nm) is too low to absorb the energy of laser, resulting in most energy of laser is transferred into substrate and no defect is created. At the same excitation, hBN flakes have much stronger fluorescence than monolayers (Fig. 5.5a, b, d, e and f), indicating that it is easier to create color centers in hBN flakes than monolayer.

Fig. 5.5 Generation of localized color centers in hBN monolayers. (a-c) and flakes(d-g). (a,b) PL mapping images from hBN monolayers after laser irradiation. Inset: a corresponding PL spectrum in (a). (c) Corresponding microscope image of (a,b), and the implemented laser powers are: 1.25 W, 0.89 W, 0.53 W, 0.27 W and 0.10 W from right to left. (d,e,f) PL intensity mapping of laser irradiated regions in hBN flakes. Inset: the PL spectrum of (f). (g) Corresponding microscope image of (d,e,f), and the implemented laser powers are: 1.60 W, 1.25 W, 0.89 W, 0.53 W, 0.27 W and 0.10 W from left to right. Scale bar: 10 μ m.

From Fig. 5.5d, e and f, plenty of separate bright colorful spots were created after laser processing, of which the majority are attributed to single defects hosted by hBN flakes. Fig. 5.6 presents the lowest and highest $g^{(2)}(0)$ among all measured single photon emitters in hBN flakes with corresponding PL images. Each spot is measured at room temperature using a 40 μ W excitation laser with an acquisition time of 20 s and were normalized (without background correction). The fitting reveals the values of $g^{(2)}(0)$ ranges from 0.20 to 0.42 among all single photon emitters in hBN flakes in Fig. 5.5g. The fitted values of τ_{tot} in Fig. 5.6a and b are 3.4 ns and 3.2 ns, respectively. Fig. 5.6c and d show the diameter of bright spot is ~ 650 nm which is the diffraction limitation of CCD camera, indicating true diffraction limited optical center is successfully induced. The bright spot in Fig. 5.5f also demonstrates single photon emission with $g^{(2)}(0) = 0.25$, indicating one single photon emitter can be deterministically engineered by laser processing without damaging substrate. The purity of single photon emission can be improved by using high quality hBN substrate like high quality single crystals[203] and also utilizing controllable technique like strain control[204] to precisely engineer the defects in hBN.

Fig. 5.6 Single photon emitters in hBN flakes. (a,b) Second order correlation functions curves from single quantum emitter in hBN flakes. (c,d) PL images corresponding to (a) and (b). Scale bar: 1 μm .

5.4 Conclusion

In conclusion, we successfully created color centers in hBN monolayers and flakes via laser irradiation and find the transformation from hBN to cBN at large hBN monolayers region. The strong and sharp emission matches well with that of $\text{N}_\text{B}\text{V}_\text{N}$ like point defects in hBN. Laser processed hBN flakes intends to exhibit sharper emission, brighter color centers and better single photon emissions compared with monolayers. Our results offer a new approach to engineering defects in hBN and motivate more endeavors to explore further the optical properties of 2D materials in the application of photonics and quantum technology using laser irradiation.

Chapter 6 Conclusion

In this thesis, we studied the photonic environment changes in emitters induced by various optical cavities ranging from photonic crystals and plasmonic nanocavities. Photon emitters experienced a photonic environment change from broadband confinement in photonic crystals to extreme field confinement in gap plasmonic nanocavities. The light-matter interaction results in light energy redistribution of photonic crystals at weak coupling regime, and Rabi splitting in nanocavities at strong coupling regime.

We have successfully fabricated perovskite photonic crystals with EBL and RIE techniques and observed strong light redistribution and inhibition concurrently. Compared to unpatterned perovskite films, the light spontaneous emission rate of perovskite photonic crystals is greatly inhibited by 7.9 folds due to photonic bandgap effect, and simultaneously PL intensity is largely enhanced by a factor of 23.5, implying high extraction efficiency. When scaling down the size of both optical cavities with plasmonic nanocavities and emitters with MoS₂ monolayer, the light-matter interaction experienced a transition from weak coupling regime with 1570-fold PL intensity enhancement to strong coupling regime with Rabi splitting as large as 190 meV. The formation of polariton states in NCoM is attributed to the collaborative effect of large exciton binding energy in MoS₂ monolayer, ultra-small mode volume and ultra-strong optical mode confinement in NCoM. Both the experimental and theoretical studies performed here provide a new guideline for selecting suitable plasmonic nanostructures to implement strong coupling operation.

We further decreased the size of emitters by engineering single photon sources in hBN monolayers and flakes via laser irradiation. The strong and sharp emission matches well with that of N_BV_N point defects in hBN. Laser processed hBN flakes intends to exhibit sharper emission, brighter

color centers and better single photon emissions compared with monolayers. Even the strong coupling of individual quantum emitters hasn't been realized in this thesis, the plasmonic nanocavities provide an effective platform to engineer photonic environment around single photon sources.

Overall, photonic crystals provide a platform which can largely modify the modes inside the film and enhance the extraction efficiency while the plasmonic nanocavities provide a stronger optical field confinement and can even improve the light matter interaction from weak coupling to strong coupling. Both have their unique advantages but suffer from some shortcomings. Photonic crystals nanocavities are usually made of dielectric materials and have low loss. However, the performance of photonic crystals cavities are limited by the difficulty of reducing the volume[107]. In contrast, plasmonic nanocavities show improved confinement with smaller volume but suffer from metal absorption loss. To improve the performance of single photon sources in hBN, I personally believe plasmonic nanocavities are better candidates. As an atomic layer, the incorporation of hBN into plasmonic nanocavities will have little effect on the physical mode and thus, can make the best use of plasmonic nanocavities. And more importantly, the quenching effect in gap plasmonic nanocavities can be quenched due to mode hybridization, which can massively enhance emitter excitation and decay via radiative channels[205, 206].

Chapter 7 Future Directions and Outlook

7.1 Modifying Spontaneous Emission of Quantum Emitters Using Nanoparticle Resonators

Single photon sources (SPSs) are an important physical system for emergent quantum technologies, including quantum metrology, information processing, computing, and communications. For most applications, a stable, room-temperature, electrically driven and Purcell-enhanced SPS is a fundamental key towards fast and efficient quantum telecommunication in scalable nanophotonic circuit chips. Among all SPSs, hBN is one of the most promising candidates due to its flexibility for circuit integration and room temperature operation. Unlike diamond, nitride-based systems can be grown on silicon and sustain single photon emission at high temperatures. In terms of spectral range, they allow emission from visible to ultraviolet. There are sparse reports on SPS in the blue and ultraviolet spectral range although it may bring new avenues for telecommunication and lighting, particularly light fidelity.

However, in this tiny light source with a dimension smaller than the emission wavelength, light confinement is weak and the coupling with the external photonic nanostructures is necessary to optimize the confinement. For example, the operation of single photon emitters at high frequency require the fast radiative rates and high extraction efficiency.

To enhance the brightness of quantum emitter (QE), a number of approaches have been developed to increase the photonic density of states in the vicinity of the QE. Dielectric resonators[207] and plasmonic nanoantenna[208] are mostly used to engineer the photonic environment of QE. Despite of complicated fabrication processes and difficulty in tuning quality factors in dielectric resonators,

the high quality factor can boost the interaction time between the photon and field, leading to longer photon storage time and limiting the spontaneous emission rate fastening[209].

Here, one perspective way is to couple QE in hBN flakes with silver nanoparticle antenna (NPA). We observed 2.4 enhancement of fluorescence intensity in experiment, which is reasonably consist with the simulated 5.7 folds enhancement of electric field. Moreover, we also found that the spontaneous emission radiation pattern in QE is also modified by silver nanoantenna, contributing to a higher extraction efficiency and limiting the spontaneous emission rate fastening[209].

Fig. 7.1 Schematic view of NPA-QE construct consisting of a silver nanoparticle antenna and hBN flakes. The QE emission in hBN is accelerated when coupled to the plasmonic nanocube mode. Inset shows the electron micrograph of silver nanocubes with scale bar of 500 nm.

Fig. 7.1 shows the illustration of NPA-QE construct with a silver nanocube positioned over QE in hBN flakes. The size of silver nanocube is around 85 nm, giving a board plasmonic resonance around 583 nm in scattering spectrum. To quantitatively analyze the effect of NPA on QE in hBN,

we conducted a series of fluorescence measurements on QE in hBN with and without NPA. A continuous wave 532 nm laser is used to excite QE in hBN and the fluorescence signal is collected into a photodetector. Fig. 7.2 demonstrates the fluorescence enhancement of QE in hBN coupled to NPA. The NPA scattering resonance well matches the emission hBN and the emission is enhanced by almost 2.4 times after coupled to NPA. This enhancement can be easily understood by FDTD simulation. Fig. 7.3 shows the distributions of normalized electric field intensities, with enhanced electromagnetic field near the NPA. The observed fluorescence increasing of 2.4 times is in reasonable agreement with a 5.7 folds enhancement of spontaneous radiative emission rate in modelling. Besides the enhancement, the radiation field is also modified with a directional radiating pattern. The optical QE on glass gives a sphere radiation pattern while it is modified by NPA with an emission angular pattern concentrated to a critical angle into the air. The results of modified radiation pattern also give rise to the collection efficiency of QE in hBN. The results shown here demonstrate an enhanced emission rate by 5.7 and yet modification of radiation pattern with high extraction efficiency. To further enhance, confine, couple, and utilize the light at single-emitter level, plasmonic nanocavities made of noble metallic nanostructures is one of the effective ways to boost the enhancement. As presented in chapter 4, the mode volume and field enhancement of gap nanocavities can be tuned by adjusting the gap thickness. Instead of nanocube on gold mirror, gold nanosphere on gold mirror provides much stronger confinement with even smaller mode volume, thus, a better platform for strong coupling[107, 210]. Another alternative way is to couple quantum emitters with photonic crystals cavities to facilitate the emission of single photons[211]. Photonic crystals are periodic composites that allow one to engineer the propagation of photons and its fabrication technique has been well established using EBL. Photonic crystals cavities offer a platform to engineer spontaneous emission of emitters with low loss. However, a

key challenge for these two platforms is the alignment between quantum emitters and cavities. To address this problem, we can use AFM to precisely manipulate the position of nanoparticles and it has been shown that nanoparticles and nanorods can be reliably positioned on a surface by pushing them with the tip of an AFM[212, 213].

Fig. 7.2 Fluorescence enhancement of QE coupled to NPA. PL spectrum of QE-NPA and QE. Shaded area is the dark scattering spectrum of single NPA.

Fig. 7.3 Near field logarithmic electric field intensity distributions for the QE and QE-NPA.

7.2 Strong Coupling in Gap Plasmonic Nanocavities at Single Photon Level

Approaching quantum limit of strong coupling at single photon level not only reveals the quantum electrodynamics, but gives rise to advanced applications including quantum communication[11, 18] and quantum networking[9, 10]. Although strong coupling has been realized at quantum optics limit recently in quantum dots[214] and molecules[215], it has been never achieved in quantum emitters in hBN. A promising alternative to approach strong coupling beyond quantum limit is using plasmonic nanocavities featured with sub-nanometer gaps.

Fig. 7.4 Emitters coupled with plasmonic nanocavities. (a) Emitters of quantum dots, dye molecules, organic molecules and 2D monolayers. (b) Gap thickness dependence of spontaneous emission rate. (c) Quantum yield of a dipole incorporated in the gap of a gold sphere on mirror as a function of gap size. (d) Strong coupling seen in scattering spectra of individual NPoM. Adapted from REF[216], © 2019 Springer Nature Limited.

By placing emitters into strongly confined electromagnetic field, modification of absorption and radiation patterns can be realized, which can result in strong light-matter interaction. The integration can be flexible with various materials, such as quantum dots[217], molecules[146], and monolayers[218] (Fig. 7.4). The nanoscale size of the emitter and the orientation of dipole moment is essential to yield precise emitter coupling to the plasmon in the local fields of nanogap.

The high local field intensity in nanogap offers the promise of tailoring the spontaneous emission of emitters. In weak coupling regime, balancing the trade-off between light field enhancement and nonradiative channel enables the observation of fluorescence enhancement with modified spontaneous emission rates. However, for single photon emitters in hBN, with large oscillator strength, the strong light-matter interaction might be realized when embedded in gap nanocavities.

Publications List

- [1] Junhong Yu[#], [Songyan Hou](#)[#], Manoj Sharma, Landobasa YM Tobing, Zhigang Song, Savas Delikanli, Chathuranga Hettiarachchi, Daohua Zhang, Weijun Fan, Muhammad Danang Birowosuto, Hong Wang, Hilmi Volkan Demir, Cuong Dang. *Ultra-strong light-matter interaction with colloidal quantum wells in a plasmonic nanocavity. submitted* ([#]: contribute equally)
- [2] [Songyan Hou](#), Xingli Wang, Landobasa Tobing, Zhenwei Xie, Junhong Yu, Jin Zhou, Daohua Zhang, Cuong Dang, Philippe Coquet, Beng Kang Tay, Muhammad Birowosuto, Edwin Teo, Hong Wang. *Manipulating Coherent Light Matter Interaction: Continuous Transition between Strong Coupling and Weak Coupling in MoS2 Monolayer Coupled with Plasmonic Nanocavities. Advanced Optical Materials*
- [3] [Songyan Hou](#), Aozhen Xie, Zhenwei Xie, Landobasa Y.M. Tobing, Jin Zhou, Liliana Tjahjana, Junhong Yu, Chathuranga Hettiarachchi, Daohua Zhang, Cuong Dang, Edwin Hang Tong Teo, Muhammad Danang Birowosuto, and Hong Wang. *Concurrent Inhibition and Redistribution of Spontaneous Emission from All Inorganic Perovskite Photonic Crystals. ACS Photonics (Cover)*
- [4] [Songyan Hou](#), Muhammad Danang Birowosuto, Saleem Umar, Maurice Ange Anicet, Roland Yingjie Tay, Philippe Coquet, Beng Kang Tay, Hong Wang, Edwin Hang Tong Teo. *Localized emission from laser-irradiated defects in 2D hexagonal boron nitride. 2D Materials*
- [5] Junhong Yu, Sushant Shendre, Weon-kyu Koh, Baiquan Liu, Mingjie Li, [Songyan Hou](#), Chathuranga Hettiarachchi, Savas Delikanli, Pedro Hernández-Martínez, Muhammad Danang Birowosuto, Hong Wang, Tze-Chien Sum, Hilmi Volkan Demir, Cuong Dang. *Electrically control amplified spontaneous emission in colloidal quantum dots. Science Advances*

- [6] Zhu, Minmin, Du, Zehui, Ye, Pengcheng, Li, Hongling, [Hou, Songyan](#), Tay, Roland Yingjie, Lin, Jinjun, Jing, Lin, Tsang, Siu Hon, Teo, Edwin. *Unprecedented Stretchability and Giant Enhanced Photoresponsivity Arising from BN Quantum Dots-Decorated P(VDF-TrFE) Nanofiber Photodetectors.* **under review**
- [7] Minmin Zhu, Bensong Chen, Zehui Du, Chongwei Tan, Zhikai Ng, Zhilin Ngoh, Soonsiang Chng, [Songyan Hou](#), Roland Yingjie Tay, Jinjun Lin, Siuhon Tsang, Edwin Hang Tong Teo. *Thermal boundary resistance of millimeter long VACNT arrays in contact with SnZn alloys and evidence of thermal rectifier.* **under review**
- [8] Arramel, Hu Pan, Aozhen Xie, [Songyan Hou](#), Xinmao Yin, Chi Sin Tang, Nguyen T Hoa, Muhammad D Birowosuto, Hong Wang, Cuong Dang, Andrivo Rusydi, Andrew TS Wee, Jishan Wu. *Surface molecular doping of all-inorganic perovskite using zethrenes molecules.* **Nano Research**
- [9] Umar Saleem, Muhammad Danang Birowosuto, [Songyan Hou](#), Ange Maurice, Tay Beng Kang, Edwin Hang Tong Teo, Maria Tchernycheva, Noelle Gogneau, Hong Wang. *Light emission from localized point defects induced in GaN crystal by a femtosecond-pulsed laser.* **Optical Materials Express**

Bibliography

- [1] G. Scalari *et al.*, "Ultrastrong coupling of the cyclotron transition of a 2D electron gas to a THz metamaterial," *Science*, vol. 335, no. 6074, pp. 1323-1326, 2012.
- [2] H. Mabuchi and A. Doherty, "Cavity quantum electrodynamics: coherence in context," *Science*, vol. 298, no. 5597, pp. 1372-1377, 2002.
- [3] B. E. Saleh and M. C. Teich, *Fundamentals of photonics*. John Wiley & sons, 2019.
- [4] M. Grätzel, "Photoelectrochemical cells," *nature*, vol. 414, no. 6861, p. 338, 2001.
- [5] D. A. Steigerwald *et al.*, "Illumination with solid state lighting technology," *IEEE journal of selected topics in quantum electronics*, vol. 8, no. 2, pp. 310-320, 2002.
- [6] N. T. Fofang, N. K. Grady, Z. Fan, A. O. Govorov, and N. J. Halas, "Plexciton dynamics: exciton-plasmon coupling in a J-aggregate-Au nanoshell complex provides a mechanism for nonlinearity," *Nano Letters*, vol. 11, no. 4, pp. 1556-1560, 2011.
- [7] W. Zhang, A. O. Govorov, and G. W. Bryant, "Semiconductor-metal nanoparticle molecules: Hybrid excitons and the nonlinear Fano effect," *Physical review letters*, vol. 97, no. 14, p. 146804, 2006.
- [8] A. Manjavacas, F. J. García de Abajo, and P. Nordlander, "Quantum plexcitonics: strongly interacting plasmons and excitons," *nano letters*, vol. 11, no. 6, pp. 2318-2323, 2011.
- [9] C. Monroe, "Quantum information processing with atoms and photons," *Nature*, vol. 416, no. 6877, p. 238, 2002.
- [10] K. Hennessy *et al.*, "Quantum nature of a strongly coupled single quantum dot-cavity system," *Nature*, vol. 445, no. 7130, p. 896, 2007.
- [11] H.-K. Lo and H. F. Chau, "Unconditional security of quantum key distribution over arbitrarily long distances," *science*, vol. 283, no. 5410, pp. 2050-2056, 1999.
- [12] E. M. Purcell, "Spontaneous emission probabilities at radio frequencies," in *Confined electrons and photons*: Springer, 1995, pp. 839-839.
- [13] H. Iwase, D. Englund, and J. Vučković, "Analysis of the Purcell effect in photonic and plasmonic crystals with losses," *Optics express*, vol. 18, no. 16, pp. 16546-16560, 2010.
- [14] M. Hertzog, M. Wang, J. Mony, and K. Börjesson, "Strong light-matter interactions: a new direction within chemistry," *Chemical Society Reviews*, 10.1039/C8CS00193F vol. 48, no. 3, pp. 937-961, 2019.
- [15] E. T. Jaynes and F. W. Cummings, "Comparison of quantum and semiclassical radiation theories with application to the beam maser," *Proceedings of the IEEE*, vol. 51, no. 1, pp. 89-109, 1963.
- [16] B. Rousseaux, D. G. Baranov, T. J. Antosiewicz, T. Shegai, and G. Johansson, "Strong coupling out of the blue: an interplay of quantum emitter hybridization with plasmonic dark and bright modes," *arXiv preprint arXiv:1910.08150*, 2019.
- [17] J. Hopfield, "Theory of the contribution of excitons to the complex dielectric constant of crystals," *Physical Review*, vol. 112, no. 5, p. 1555, 1958.
- [18] T. Yoshie *et al.*, "Vacuum Rabi splitting with a single quantum dot in a photonic crystal nanocavity," *Nature*, vol. 432, no. 7014, p. 200, 2004.
- [19] J. P. Reithmaier *et al.*, "Strong coupling in a single quantum dot-semiconductor microcavity system," *Nature*, vol. 432, no. 7014, p. 197, 2004.

- [20] J. Gérard, B. Sermage, B. Gayral, B. Legrand, E. Costard, and V. Thierry-Mieg, "Enhanced spontaneous emission by quantum boxes in a monolithic optical microcavity," *Physical review letters*, vol. 81, no. 5, p. 1110, 1998.
- [21] B. Gayral, J. Gérard, A. Lemaitre, C. Dupuis, L. Manin, and J. Pelouard, "High-Q wet-etched GaAs microdisks containing InAs quantum boxes," *Applied physics letters*, vol. 75, no. 13, pp. 1908-1910, 1999.
- [22] K. Djordjev, S.-J. Choi, S.-J. Choi, and R. Dapkus, "Microdisk tunable resonant filters and switches," *IEEE Photonics Technology Letters*, vol. 14, no. 6, pp. 828-830, 2002.
- [23] P. Rabiei, W. H. Steier, C. Zhang, and L. R. Dalton, "Polymer micro-ring filters and modulators," *Journal of lightwave technology*, vol. 20, no. 11, p. 1968, 2002.
- [24] K. Srinivasan, P. E. Barclay, O. Painter, J. Chen, A. Y. Cho, and C. Gmachl, "Experimental demonstration of a high quality factor photonic crystal microcavity," *Applied Physics Letters*, vol. 83, no. 10, pp. 1915-1917, 2003.
- [25] C. Hood, T. Lynn, A. Doherty, A. Parkins, and H. Kimble, "The atom-cavity microscope: Single atoms bound in orbit by single photons," *Science*, vol. 287, no. 5457, pp. 1447-1453, 2000.
- [26] D. Vernooy, V. S. Ilchenko, H. Mabuchi, E. Streed, and H. Kimble, "High-Q measurements of fused-silica microspheres in the near infrared," *Optics letters*, vol. 23, no. 4, pp. 247-249, 1998.
- [27] D. Armani, T. Kippenberg, S. Spillane, and K. Vahala, "Ultra-high-Q toroid microcavity on a chip," *Nature*, vol. 421, no. 6926, p. 925, 2003.
- [28] K. J. Vahala, "Optical microcavities," *nature*, vol. 424, no. 6950, p. 839, 2003.
- [29] L. Cao, J. S. White, J.-S. Park, J. A. Schuller, B. M. Clemens, and M. L. Brongersma, "Engineering light absorption in semiconductor nanowire devices," *Nature materials*, vol. 8, no. 8, p. 643, 2009.
- [30] P. Spinelli, M. Verschuuren, and A. Polman, "Broadband omnidirectional antireflection coating based on subwavelength surface Mie resonators," *Nature communications*, vol. 3, p. 692, 2012.
- [31] V. Menon, "Nanolasers: Lasing from 2D atomic crystals," *Nature materials*, vol. 14, no. 4, p. 370, 2015.
- [32] Y. Gao *et al.*, "High-Speed Electro-Optic Modulator Integrated with Graphene-Boron Nitride Heterostructure and Photonic Crystal Nanocavity," *Nano Letters*, vol. 15, no. 3, pp. 2001-2005, 2015/03/11 2015.
- [33] A. Goban *et al.*, "Superradiance for atoms trapped along a photonic crystal waveguide," *Physical review letters*, vol. 115, no. 6, p. 063601, 2015.
- [34] J. D. Joannopoulos, S. G. Johnson, J. N. Winn, and R. D. Meade, "Molding the flow of light," *Princeton Univ. Press, Princeton, NJ [ua]*, 2008.
- [35] R. Coccioli, M. Boroditsky, K. Kim, Y. Rahmat-Samii, and E. Yablonovitch, "Smallest possible electromagnetic mode volume in a dielectric cavity," *IEE Proceedings-Optoelectronics*, vol. 145, no. 6, pp. 391-397, 1998.
- [36] R. H. Ritchie, "Plasma Losses by Fast Electrons in Thin Films," *Physical Review*, vol. 106, no. 5, pp. 874-881, 06/01/ 1957.
- [37] H. U. Yang, J. D'Archangel, M. L. Sundheimer, E. Tucker, G. D. Boreman, and M. B. Raschke, "Optical dielectric function of silver," *Physical Review B*, vol. 91, no. 23, p. 235137, 2015.

- [38] W. L. Barnes, A. Dereux, and T. W. Ebbesen, "Surface plasmon subwavelength optics," *Nature*, vol. 424, no. 6950, pp. 824-830, 2003/08/01 2003.
- [39] M. A. Ordal, R. J. Bell, R. W. Alexander, L. L. Long, and M. R. Querry, "Optical properties of fourteen metals in the infrared and far infrared: Al, co, cu, au, fe, pb, mo, ni, pd, pt, ag, ti, v, and w," *Applied optics*, vol. 24, no. 24, pp. 4493-4499, 1985.
- [40] R. Chance, A. Prock, and R. Silbey, "Molecular fluorescence and energy transfer near interfaces," *Adv. Chem. Phys.*, vol. 37, pp. 1-65, 1978.
- [41] G. W. Ford and W. H. Weber, "Electromagnetic interactions of molecules with metal surfaces," *Physics Reports*, vol. 113, no. 4, pp. 195-287, 1984.
- [42] P. Muehlschlegel, H.-J. Eisler, O. J. Martin, B. Hecht, and D. Pohl, "Resonant optical antennas," *science*, vol. 308, no. 5728, pp. 1607-1609, 2005.
- [43] E. Hutter and J. H. Fendler, "Exploitation of Localized Surface Plasmon Resonance," *Advanced Materials*, vol. 16, no. 19, pp. 1685-1706, 2004.
- [44] M. L. Juan, M. Righini, and R. Quidant, "Plasmon nano-optical tweezers," *Nature photonics*, vol. 5, no. 6, p. 349, 2011.
- [45] J. Olson, S. Dominguez-Medina, A. Hoggard, L.-Y. Wang, W.-S. Chang, and S. Link, "Optical characterization of single plasmonic nanoparticles," *Chemical Society Reviews*, 10.1039/C4CS00131A vol. 44, no. 1, pp. 40-57, 2015.
- [46] R. Chikkaraddy *et al.*, "Single-molecule strong coupling at room temperature in plasmonic nanocavities," *Nature*, vol. 535, no. 7610, p. 127, 2016.
- [47] K. S. Novoselov, V. Fal, L. Colombo, P. Gellert, M. Schwab, and K. Kim, "A roadmap for graphene," *nature*, vol. 490, no. 7419, p. 192, 2012.
- [48] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, and H. Zhang, "The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets," *Nature chemistry*, vol. 5, no. 4, p. 263, 2013.
- [49] K. K. Kim *et al.*, "Synthesis of monolayer hexagonal boron nitride on Cu foil using chemical vapor deposition," *Nano letters*, vol. 12, no. 1, pp. 161-166, 2011.
- [50] K.-K. Liu *et al.*, "Growth of large-area and highly crystalline MoS₂ thin layers on insulating substrates," *Nano letters*, vol. 12, no. 3, pp. 1538-1544, 2012.
- [51] Y. Zhan, Z. Liu, S. Najmaei, P. M. Ajayan, and J. Lou, "Large-area vapor-phase growth and characterization of MoS₂ atomic layers on a SiO₂ substrate," *Small*, vol. 8, no. 7, pp. 966-971, 2012.
- [52] Y. H. Lee *et al.*, "Synthesis of large-area MoS₂ atomic layers with chemical vapor deposition," *Advanced materials*, vol. 24, no. 17, pp. 2320-2325, 2012.
- [53] Y.-C. Lin *et al.*, "Wafer-scale MoS₂ thin layers prepared by MoO₃ sulfurization," *Nanoscale*, vol. 4, no. 20, pp. 6637-6641, 2012.
- [54] Y. Cao *et al.*, "Perovskite light-emitting diodes based on spontaneously formed submicrometre-scale structures," *Nature*, vol. 562, no. 7726, pp. 249-253, 2018/10/01 2018.
- [55] X. Li *et al.*, "All inorganic halide perovskites nanosystem: synthesis, structural features, optical properties and optoelectronic applications," *Small*, vol. 13, no. 9, p. 1603996, 2017.
- [56] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, and S. I. Seok, "Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells," *Nano letters*, vol. 13, no. 4, pp. 1764-1769, 2013.
- [57] X. Zhang *et al.*, "Enhancing the brightness of cesium lead halide perovskite nanocrystal based green light-emitting devices through the interface engineering with perfluorinated ionomer," *Nano letters*, vol. 16, no. 2, pp. 1415-1420, 2016.

- [58] N. K. Kumawat, A. Dey, K. Narasimhan, and D. Kabra, "Near infrared to visible electroluminescent diodes based on organometallic halide perovskites: structural and optical investigation," *ACS photonics*, vol. 2, no. 3, pp. 349-354, 2015.
- [59] G. Li *et al.*, "Efficient light-emitting diodes based on nanocrystalline perovskite in a dielectric polymer matrix," *Nano letters*, vol. 15, no. 4, pp. 2640-2644, 2015.
- [60] S. Hou *et al.*, "Localized emission from laser-irradiated defects in 2D hexagonal boron nitride," *2D Materials*, vol. 5, no. 1, p. 015010, 2017.
- [61] F. Timpu, A. Sergeyev, N. R. Hendricks, and R. Grange, "Second-harmonic enhancement with Mie resonances in perovskite nanoparticles," *Acs Photonics*, vol. 4, no. 1, pp. 76-84, 2016.
- [62] S. Chen *et al.*, "A photonic crystal laser from solution based organo-lead iodide perovskite thin films," *Acs Nano*, vol. 10, no. 4, pp. 3959-3967, 2016.
- [63] G. Xing *et al.*, "Low-temperature solution-processed wavelength-tunable perovskites for lasing," *Nature materials*, vol. 13, no. 5, p. 476, 2014.
- [64] B. R. Sutherland and E. H. Sargent, "Perovskite photonic sources," *Nature Photonics*, vol. 10, no. 5, p. 295, 2016.
- [65] H. Zhu *et al.*, "Lead halide perovskite nanowire lasers with low lasing thresholds and high quality factors," *Nature materials*, vol. 14, no. 6, pp. 636-642, 2015.
- [66] J. H. Burroughes *et al.*, "Light-emitting diodes based on conjugated polymers," *nature*, vol. 347, no. 6293, pp. 539-541, 1990.
- [67] N. Tessler, G. Denton, and R. Friend, "Lasing from conjugated-polymer microcavities," *Nature*, vol. 382, no. 6593, pp. 695-697, 1996.
- [68] S. Das *et al.*, "High-performance flexible perovskite solar cells by using a combination of ultrasonic spray-coating and low thermal budget photonic curing," *Acs Photonics*, vol. 2, no. 6, pp. 680-686, 2015.
- [69] M. Fujita, S. Takahashi, Y. Tanaka, T. Asano, and S. Noda, "Simultaneous inhibition and redistribution of spontaneous light emission in photonic crystals," *Science*, vol. 308, no. 5726, pp. 1296-1298, 2005.
- [70] J. J. Wierer Jr, A. David, and M. M. Megens, "III-nitride photonic-crystal light-emitting diodes with high extraction efficiency," *Nature Photonics*, vol. 3, no. 3, p. 163, 2009.
- [71] P. Lodahl *et al.*, "Controlling the dynamics of spontaneous emission from quantum dots by photonic crystals," *Nature*, vol. 430, no. 7000, p. 654, 2004.
- [72] D. Englund *et al.*, "Controlling the spontaneous emission rate of single quantum dots in a two-dimensional photonic crystal," *Physical review letters*, vol. 95, no. 1, p. 013904, 2005.
- [73] E. Yablonovitch, "Inhibited spontaneous emission in solid-state physics and electronics," *Physical review letters*, vol. 58, no. 20, p. 2059, 1987.
- [74] S. Fan, P. R. Villeneuve, J. Joannopoulos, and E. Schubert, "High extraction efficiency of spontaneous emission from slabs of photonic crystals," *Physical review letters*, vol. 78, no. 17, p. 3294, 1997.
- [75] Y. Tian *et al.*, "Highly Efficient Spectrally Stable Red Perovskite Light-Emitting Diodes," *Advanced Materials*, vol. 30, no. 20, p. 1707093, 2018.
- [76] S. V. Makarov *et al.*, "Multifold emission enhancement in nanoimprinted hybrid perovskite metasurfaces," *ACS Photonics*, vol. 4, no. 4, pp. 728-735, 2017.
- [77] S. Schünemann, S. Brittman, K. Chen, E. C. Garnett, and H. Tüysüz, "Halide Perovskite 3D Photonic Crystals for Distributed Feedback Lasers," *ACS Photonics*, vol. 4, no. 10, pp. 2522-2528, 2017.

- [78] Y. F. Ng *et al.*, "Rapid Crystallization of All-Inorganic CsPbBr₃ Perovskite for High-Brightness Light-Emitting Diodes," *ACS Omega*, vol. 2, no. 6, pp. 2757-2764, 2017.
- [79] L. Zhang *et al.*, "Ultra-bright and highly efficient inorganic based perovskite light-emitting diodes," *Nature Communications*, Article vol. 8, p. 15640, 06/07/online 2017.
- [80] K. Lin *et al.*, "Perovskite light-emitting diodes with external quantum efficiency exceeding 20 per cent," *Nature*, vol. 562, no. 7726, pp. 245-248, 2018/10/01 2018.
- [81] J. J. Wierer Jr, A. David, and M. M. Megens, "III-nitride photonic-crystal light-emitting diodes with high extraction efficiency," *Nature Photonics*, Article vol. 3, p. 163, 02/22/online 2009.
- [82] X. Zhao, J. D. A. Ng, R. H. Friend, and Z.-K. Tan, "Opportunities and Challenges in Perovskite Light-Emitting Devices," *ACS Photonics*, vol. 5, no. 10, pp. 3866-3875, 2018.
- [83] C.-Y. Huang *et al.*, "CsPbBr₃ perovskite quantum dot vertical cavity lasers with low threshold and high stability," *ACS Photonics*, vol. 4, no. 9, pp. 2281-2289, 2017.
- [84] S. Chen and A. Nurmikko, "Stable Green Perovskite Vertical-Cavity Surface-Emitting Lasers on Rigid and Flexible Substrates," *ACS Photonics*, vol. 4, no. 10, pp. 2486-2494, 2017.
- [85] B. Johs and J. S. Hale, "Dielectric function representation by B-splines," *physica status solidi (a)*, vol. 205, no. 4, pp. 715-719, 2008.
- [86] Z. Zhang, L. Zhang, M. N. Hedhili, H. Zhang, and P. Wang, "Plasmonic gold nanocrystals coupled with photonic crystal seamlessly on TiO₂ nanotube photoelectrodes for efficient visible light photoelectrochemical water splitting," *Nano letters*, vol. 13, no. 1, pp. 14-20, 2012.
- [87] K. Kempa *et al.*, "Photonic crystals based on periodic arrays of aligned carbon nanotubes," *Nano Letters*, vol. 3, no. 1, pp. 13-18, 2003.
- [88] D. Liu, C. Yang, M. Bates, and R. R. Lunt, "Room-Temperature Processing of Inorganic Perovskite Films to Enable Flexible Solar Cells," *arXiv preprint arXiv:1806.06855*, 2018.
- [89] B. Gholipour *et al.*, "Organometallic perovskite metasurfaces," *Advanced Materials*, vol. 29, no. 9, p. 1604268, 2017.
- [90] N. Klein-Kedem, D. Cahen, and G. Hodes, "Effects of Light and Electron Beam Irradiation on Halide Perovskites and Their Solar Cells," *Accounts of Chemical Research*, vol. 49, no. 2, pp. 347-354, 2016/02/16 2016.
- [91] J. Ran, O. O. Dyck, X. Wang, B. Yang, D. B. Geohegan, and K. Xiao, "Electron-Beam-Related Studies of Halide Perovskites: Challenges and Opportunities," *Advanced Energy Materials*, vol. n/a, no. n/a, p. 1903191.
- [92] L. s. Ondič, K. i. Dohnalová, M. Ledinský, A. Kromka, O. Babchenko, and B. Rezek, "Effective extraction of photoluminescence from a diamond layer with a photonic crystal," *ACS nano*, vol. 5, no. 1, pp. 346-350, 2010.
- [93] K. McGroddy *et al.*, "Directional emission control and increased light extraction in GaN photonic crystal light emitting diodes," *Applied physics letters*, vol. 93, no. 10, p. 103502, 2008.
- [94] Q. Wang, S. Stobbe, and P. Lodahl, "Mapping the local density of optical states of a photonic crystal with single quantum dots," *Physical review letters*, vol. 107, no. 16, p. 167404, 2011.
- [95] Y. R. Do *et al.*, "Enhanced light extraction from organic light-emitting Diodes with 2D SiO₂/SiN_x photonic crystals," *Advanced Materials*, vol. 15, no. 14, pp. 1214-1218, 2003.

- [96] A. Mahdavi, G. Sarau, J. Xavier, T. K. Paraíso, S. Christiansen, and F. Vollmer, "Maximizing photoluminescence extraction in silicon photonic crystal slabs," *Scientific reports*, vol. 6, p. 25135, 2016.
- [97] K. Vynck, M. Burrelli, F. Riboli, and D. S. Wiersma, "Photon management in two-dimensional disordered media," *Nature materials*, vol. 11, no. 12, p. 1017, 2012.
- [98] A. Chutinan, N. P. Kherani, and S. Zukotynski, "High-efficiency photonic crystal solar cell architecture," *Optics Express*, vol. 17, no. 11, pp. 8871-8878, 2009/05/25 2009.
- [99] C. Schneider *et al.*, "An electrically pumped polariton laser," *Nature*, vol. 497, no. 7449, p. 348, 2013.
- [100] S. K. Rajendran, M. Wei, H. Ohadi, A. Ruseckas, G. A. Turnbull, and I. D. W. Samuel, "Low Threshold Polariton Lasing from a Solution-Processed Organic Semiconductor in a Planar Microcavity," *Adv. Opt. Mater.*, vol. 7, no. 12, p. 1801791, 18/6/2019 2019.
- [101] J. A. Hutchison *et al.*, "Tuning the Work-Function Via Strong Coupling," *Adv. Mater.*, vol. 25, no. 17, pp. 2481-2485, 2013.
- [102] M. Y. Musa *et al.*, "Confined transverse electric phonon polaritons in hexagonal boron nitrides," *2D Materials*, vol. 5, no. 1, p. 015018, 2017.
- [103] M. Fleischhauer and M. D. Lukin, "Quantum memory for photons: Dark-state polaritons," *Phys. Rev. A*, vol. 65, no. 2, p. 022314, 2002.
- [104] A. A. Houck, H. E. Türeci, and J. Koch, "On-chip quantum simulation with superconducting circuits," *Nat. Phys.*, vol. 8, no. 4, p. 292, 2012.
- [105] D. G. Lidzey, D. Bradley, M. Skolnick, T. Virgili, S. Walker, and D. Whittaker, "Strong exciton-photon coupling in an organic semiconductor microcavity," *Nature*, vol. 395, no. 6697, p. 53, 1998.
- [106] B. Lee *et al.*, "Fano resonance and spectrally modified photoluminescence enhancement in monolayer MoS₂ integrated with plasmonic nanoantenna array," *Nano letters*, vol. 15, no. 5, pp. 3646-3653, 2015.
- [107] R. Chikkaraddy *et al.*, "Single-molecule strong coupling at room temperature in plasmonic nanocavities," *Nature*, vol. 535, no. 7610, pp. 127-130, 2016.
- [108] K. F. Mak and J. Shan, "Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides," *Nature Photonics*, vol. 10, no. 4, p. 216, 2016.
- [109] A. Ramasubramaniam, "Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides," *Physical Review B*, vol. 86, no. 11, p. 115409, 2012.
- [110] D. Xiao, M.-C. Chang, and Q. Niu, "Berry phase effects on electronic properties," *Reviews of modern physics*, vol. 82, no. 3, p. 1959, 2010.
- [111] J. Feldmann *et al.*, "Linewidth dependence of radiative exciton lifetimes in quantum wells," *Physical review letters*, vol. 59, no. 20, p. 2337, 1987.
- [112] X. Xu, W. Yao, D. Xiao, and T. F. Heinz, "Spin and pseudospins in layered transition metal dichalcogenides," *Nature Physics*, vol. 10, no. 5, pp. 343-350, 2014.
- [113] J. R. Schaibley *et al.*, "Valleytronics in 2D materials," *Nat. Rev. Mater.*, vol. 1, no. 11, p. 16055, 2016.
- [114] S. Hou *et al.*, "Localized emission from laser-irradiated defects in 2D hexagonal boron nitride," *2D Mater.*, vol. 5, no. 1, p. 015010, 2017.
- [115] M. Milićević *et al.*, "Edge states in polariton honeycomb lattices," *2D Materials*, vol. 2, no. 3, p. 034012, 2015.
- [116] M.-E. Kleemann *et al.*, "Strong-coupling of WSe₂ in ultra-compact plasmonic nanocavities at room temperature," *Nat. Commun.*, vol. 8, no. 1, p. 1296, 2017.

- [117] T. Low *et al.*, "Polaritons in layered two-dimensional materials," *Nat. Mater.*, vol. 16, no. 2, p. 182, 2017.
- [118] H. Hu, J. Zhang, S. A. Maier, and Y. Luo, "Enhancing Third-Harmonic Generation with Spatial Nonlocality," *Acs Photonics*, vol. 5, no. 2, pp. 592-598, 2017.
- [119] P. Berini and I. De Leon, "Surface plasmon–polariton amplifiers and lasers," *Nat. Photonics*, vol. 6, no. 1, p. 16, 2012.
- [120] U. Saleem *et al.*, "Light emission from localised point defects induced in GaN crystal by a femtosecond-pulsed laser," *Optical Materials Express*, vol. 8, no. 9, pp. 2703-2712, 2018/09/01 2018.
- [121] J. Sun *et al.*, "Light-Emitting Plexciton: Exploiting Plasmon–Exciton Interaction in the Intermediate Coupling Regime," *ACS nano*, vol. 12, no. 10, pp. 10393-10402, 2018.
- [122] D. I. Yakubovsky, A. V. Arsenin, Y. V. Stebunov, D. Y. Fedyanin, and V. S. Volkov, "Optical constants and structural properties of thin gold films," *Optics express*, vol. 25, no. 21, pp. 25574-25587, 2017.
- [123] D. K. Gramotnev and S. I. Bozhevolnyi, "Plasmonics beyond the diffraction limit," *Nat. Photonics*, vol. 4, no. 2, p. 83, 2010.
- [124] A. Klots *et al.*, "Probing excitonic states in suspended two-dimensional semiconductors by photocurrent spectroscopy," *Sci. Rep.*, vol. 4, p. 6608, 2014.
- [125] D. Xiao, G.-B. Liu, W. Feng, X. Xu, and W. Yao, "Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides," *Phys. Rev. Lett.*, vol. 108, no. 19, p. 196802, 2012.
- [126] Y. Gong *et al.*, "Vertical and in-plane heterostructures from WS₂/MoS₂ monolayers," *Nat. Mater.*, vol. 13, no. 12, p. 1135, 2014.
- [127] J. Bellessa, C. Bonnard, J. Plenet, and J. Mugnier, "Strong coupling between surface plasmons and excitons in an organic semiconductor," *Phys. Rev. Lett.*, vol. 93, no. 3, p. 036404, 2004.
- [128] P. Törmä and W. L. Barnes, "Strong coupling between surface plasmon polaritons and emitters: a review," *Rep. Prog. Phys.*, vol. 78, no. 1, p. 013901, 2014.
- [129] M. E. Kleemann *et al.*, "Strong-coupling of WSe₂ in ultra-compact plasmonic nanocavities at room temperature," *Nat. Commun.*, vol. 8, no. 1, p. 1296, 2017.
- [130] M. Stührenberg *et al.*, "Strong Light–Matter Coupling between Plasmons in Individual Gold Bi-pyramids and Excitons in Mono- and Multilayer WSe₂," *Nano Lett.*, vol. 18, no. 9, pp. 5938-5945, 2018/09/12 2018.
- [131] S. Wang *et al.*, "Coherent Coupling of WS₂ Monolayers with Metallic Photonic Nanostructures at Room Temperature," *Nano Lett.*, vol. 16, no. 7, pp. 4368-4374, 2016/07/13 2016.
- [132] Z. Wang *et al.*, "Giant photoluminescence enhancement in tungsten-diselenide–gold plasmonic hybrid structures," *Nature communications*, vol. 7, p. 11283, 2016.
- [133] S. Wang *et al.*, "Limits to Strong Coupling of Excitons in Multilayer WS₂ with Collective Plasmonic Resonances," *ACS Photonics*, vol. 6, no. 2, pp. 286-293, 2019/02/20 2019.
- [134] W. Liu *et al.*, "Strong exciton–plasmon coupling in MoS₂ coupled with plasmonic lattice," *Nano Lett.*, vol. 16, no. 2, pp. 1262-1269, 2016.
- [135] X. Yang *et al.*, "Plasmon-exciton coupling of monolayer MoS₂-Ag nanoparticles hybrids for surface catalytic reaction," *Mater. Today Energy*, vol. 5, pp. 72-78, 2017.
- [136] M.-E. Kleemann *et al.*, "Strong-coupling of WSe₂ in ultra-compact plasmonic nanocavities at room temperature," *Nature communications*, vol. 8, no. 1, p. 1296, 2017.

- [137] X. Han, K. Wang, X. Xing, M. Wang, and P. Lu, "Rabi Splitting in a Plasmonic Nanocavity Coupled to a WS₂ Monolayer at Room Temperature," *ACS Photonics*, vol. 5, no. 10, pp. 3970-3976, 2018.
- [138] X. Liu *et al.*, "Strong light–matter coupling in two-dimensional atomic crystals," *Nature Photonics*, vol. 9, no. 1, p. 30, 2015.
- [139] W. Liu *et al.*, "Strong exciton–plasmon coupling in MoS₂ coupled with plasmonic lattice," *Nano letters*, vol. 16, no. 2, pp. 1262-1269, 2016.
- [140] X. Liu, W. Bao, Q. Li, C. Ropp, Y. Wang, and X. Zhang, "Control of coherently coupled exciton polaritons in monolayer tungsten disulphide," *Physical review letters*, vol. 119, no. 2, p. 027403, 2017.
- [141] N. Lundt *et al.*, "Room-temperature Tamm-plasmon exciton-polaritons with a WSe₂ monolayer," *Nature communications*, vol. 7, p. 13328, 2016.
- [142] M. Stührenberg *et al.*, "Strong Light–Matter Coupling between Plasmons in Individual Gold Bi-pyramids and Excitons in Mono- and Multilayer WSe₂," *Nano Letters*, vol. 18, no. 9, pp. 5938-5945, 2018/09/12 2018.
- [143] S. Wang *et al.*, "Coherent Coupling of WS₂ Monolayers with Metallic Photonic Nanostructures at Room Temperature," *Nano Letters*, vol. 16, no. 7, pp. 4368-4374, 2016/07/13 2016.
- [144] M. Geisler *et al.*, "Single-crystalline gold nanodisks on WS₂ mono- and multilayers for strong coupling at room temperature," *ACS Photonics*, 2019/03/28 2019.
- [145] T. Hoang, G. Akselrod, C. Argyropoulos, J. Huang, D. Smith, and M. Mikkelsen, "Ultrafast spontaneous emission source using plasmonic nanoantennas," *Nat. Commun.*, vol. 6, p. 7788, 2015.
- [146] G. M. Akselrod *et al.*, "Probing the mechanisms of large Purcell enhancement in plasmonic nanoantennas," *Nature Photonics*, vol. 8, no. 11, p. 835, 2014.
- [147] J. Huang, G. M. Akselrod, T. Ming, J. Kong, and M. H. Mikkelsen, "Tailored Emission Spectrum of 2D Semiconductors Using Plasmonic Nanocavities," *ACS Photonics*, vol. 5, no. 2, pp. 552-558, 2018/02/21 2018.
- [148] A. F. Koenderink, "On the use of Purcell factors for plasmon antennas," *Opt. Lett.*, vol. 35, no. 24, pp. 4208-4210, 2010/12/15 2010.
- [149] M. Palstra Isabelle, M. Doeleman Hugo, and A. F. Koenderink, "Hybrid cavity-antenna systems for quantum optics outside the cryostat?," in *Nanophotonics* vol. 0, ed, 2019.
- [150] A. K. Geim and I. V. Grigorieva, "Van der Waals heterostructures," *Nature*, vol. 499, no. 7459, pp. 419-425, 2013.
- [151] S. Z. Butler *et al.*, "Progress, challenges, and opportunities in two-dimensional materials beyond graphene," *ACS nano*, vol. 7, no. 4, pp. 2898-2926, 2013.
- [152] F. Xia, H. Wang, D. Xiao, M. Dubey, and A. Ramasubramaniam, "Two-dimensional material nanophotonics," *Nature Photonics*, vol. 8, no. 12, pp. 899-907, 2014.
- [153] D. Rajendra *et al.*, "Anisotropic charge carrier transport in free-standing hexagonal boron nitride thin films," *Applied Physics Express*, vol. 9, no. 6, p. 065801, 2016.
- [154] Y. Matthew, X. Jiamin, and B. J. LeRoy, "Graphene on hexagonal boron nitride," *Journal of Physics: Condensed Matter*, vol. 26, no. 30, p. 303201, 2014.
- [155] Z. Wenjing, W. Qixing, C. Yu, W. Zhuo, and T. S. W. Andrew, "Van der Waals stacked 2D layered materials for optoelectronics," *2D Materials*, vol. 3, no. 2, p. 022001, 2016.

- [156] L. Zhong *et al.*, "2D materials advances: from large scale synthesis and controlled heterostructures to improved characterization techniques, defects and applications," *2D Materials*, vol. 3, no. 4, p. 042001, 2016.
- [157] K. Watanabe, T. Taniguchi, and H. Kanda, "Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal," *Nature materials*, vol. 3, no. 6, pp. 404-409, 2004.
- [158] A. Rubio, J. L. Corkill, and M. L. Cohen, "Theory of graphitic boron nitride nanotubes," *Physical Review B*, vol. 49, no. 7, p. 5081, 1994.
- [159] Z. Yuanbo, R. Angel, and L. Guy Le, "Emergent elemental two-dimensional materials beyond graphene," *Journal of Physics D: Applied Physics*, vol. 50, no. 5, p. 053004, 2017.
- [160] M. Xu, T. Liang, M. Shi, and H. Chen, "Graphene-like two-dimensional materials," *Chemical reviews*, vol. 113, no. 5, pp. 3766-3798, 2013.
- [161] C. R. Dean *et al.*, "Boron nitride substrates for high-quality graphene electronics," *Nature nanotechnology*, vol. 5, no. 10, pp. 722-726, 2010.
- [162] M. J. S. Matos, M. S. C. Mazzoni, and H. Chacham, "Graphene–boron nitride superlattices: the role of point defects at the BN layer," *Nanotechnology*, vol. 25, no. 16, p. 165705, 2014.
- [163] Z. Dong, Z. Dong-Bo, Y. Fuhua, L. Hai-Qing, X. Hongqi, and C. Kai, "Interface engineering of electronic properties of graphene/boron nitride lateral heterostructures," *2D Materials*, vol. 2, no. 4, p. 041001, 2015.
- [164] Z. Jin-Cheng *et al.*, "High thermal conductivity of hexagonal boron nitride laminates," *2D Materials*, vol. 3, no. 1, p. 011004, 2016.
- [165] L. Lindsay and D. Broido, "Enhanced thermal conductivity and isotope effect in single-layer hexagonal boron nitride," *Physical Review B*, vol. 84, no. 15, p. 155421, 2011.
- [166] O. L. Krivanek *et al.*, "Atom-by-atom structural and chemical analysis by annular dark-field electron microscopy," *Nature*, vol. 464, no. 7288, pp. 571-574, 2010.
- [167] Z. Simon, M. Péter, A. F. V. Carlos, and S. Christian, "Role of hexagonal boron nitride in protecting ferromagnetic nanostructures from oxidation," *2D Materials*, vol. 3, no. 1, p. 011008, 2016.
- [168] Y. Kubota, K. Watanabe, O. Tsuda, and T. Taniguchi, "Deep ultraviolet light-emitting hexagonal boron nitride synthesized at atmospheric pressure," *Science*, vol. 317, no. 5840, pp. 932-934, 2007.
- [169] T. T. Tran, K. Bray, M. J. Ford, M. Toth, and I. Aharonovich, "Quantum emission from hexagonal boron nitride monolayers," *Nature nanotechnology*, vol. 11, no. 1, pp. 37-41, 2016.
- [170] T. T. Tran *et al.*, "Robust multicolor single photon emission from point defects in hexagonal boron nitride," *ACS nano*, vol. 10, no. 8, pp. 7331-7338, 2016.
- [171] R. Machaka, R. M. Erasmus, and T. E. Derry, "Formation of cBN nanocrystals by He⁺ implantation into hBN," *Diamond and Related Materials*, vol. 19, no. 10, pp. 1131-1134, 2010.
- [172] Y. Guo, J. Qiu, and W. Guo, "Mechanical and electronic coupling in few-layer graphene and hBN wrinkles: a first-principles study," *Nanotechnology*, vol. 27, no. 50, p. 505702, 2016.
- [173] C. Attacalite, M. Bockstedte, A. Marini, A. Rubio, and L. Wirtz, "Coupling of excitons and defect states in boron-nitride nanostructures," *Physical Review B*, vol. 83, no. 14, p. 144115, 2011.

- [174] W. Orellana and H. Chacham, "Stability of native defects in hexagonal and cubic boron nitride," *Physical Review B*, vol. 63, no. 12, p. 125205, 2001.
- [175] A. Klok, F. von Stetten, R. Zengerle, and S. Kerzenmacher, "Strategies for the fabrication of porous platinum electrodes," *Advanced Materials*, vol. 23, no. 43, pp. 4976-5008, 2011.
- [176] N. P. Dasgupta *et al.*, "25th anniversary article: semiconductor nanowires—synthesis, characterization, and applications," *Advanced materials*, vol. 26, no. 14, pp. 2137-2184, 2014.
- [177] J. McClelland, R. Scholten, E. Palm, and R. Celotta, "Laser-focused atomic deposition," *SCIENCE-NEW YORK THEN WASHINGTON*, vol. 262, pp. 877-877, 1993.
- [178] J. Jersch and K. Dickmann, "Nanostructure fabrication using laser field enhancement in the near field of a scanning tunneling microscope tip," *Applied physics letters*, vol. 68, no. 6, pp. 868-870, 1996.
- [179] X. Huang *et al.*, "Graphene-based materials: synthesis, characterization, properties, and applications," *small*, vol. 7, no. 14, pp. 1876-1902, 2011.
- [180] M. F. El-Kady, V. Strong, S. Dubin, and R. B. Kaner, "Laser scribing of high-performance and flexible graphene-based electrochemical capacitors," *Science*, vol. 335, no. 6074, pp. 1326-1330, 2012.
- [181] R. R. Gattass and E. Mazur, "Femtosecond laser micromachining in transparent materials," *Nature photonics*, vol. 2, no. 4, pp. 219-225, 2008.
- [182] A. M. Morales and C. M. Lieber, "A laser ablation method for the synthesis of crystalline semiconductor nanowires," *Science*, vol. 279, no. 5348, pp. 208-211, 1998.
- [183] Z. R. Dai, Z. W. Pan, and Z. L. Wang, "Novel nanostructures of functional oxides synthesized by thermal evaporation," *Advanced Functional Materials*, vol. 13, no. 1, pp. 9-24, 2003.
- [184] R. Buividas *et al.*, "Photoluminescence from voids created by femtosecond-laser pulses inside cubic-BN," *Optics letters*, vol. 40, no. 24, pp. 5711-5713, 2015.
- [185] Y.-C. Chen *et al.*, "Laser writing of coherent colour centres in diamond," *Nature Photonics*, 2016.
- [186] R. Y. Tay *et al.*, "Growth of large single-crystalline two-dimensional boron nitride hexagons on electropolished copper," *Nano letters*, vol. 14, no. 2, pp. 839-846, 2014.
- [187] Y. Wang *et al.*, "Electrochemical delamination of CVD-grown graphene film: toward the recyclable use of copper catalyst," *ACS nano*, vol. 5, no. 12, pp. 9927-9933, 2011.
- [188] M. D. Birowosuto *et al.*, "Fast Purcell-enhanced single photon source in 1,550-nm telecom band from a resonant quantum dot-cavity coupling," *Scientific reports*, vol. 2, 2012.
- [189] P. Michler, A. Imamoglu, M. Mason, P. Carson, G. Strouse, and S. Buratto, "Quantum correlation among photons from a single quantum dot at room temperature," *Nature*, vol. 406, no. 6799, pp. 968-970, 2000.
- [190] S. Castelletto *et al.*, "Room temperature quantum emission from cubic silicon carbide nanoparticles," *ACS nano*, vol. 8, no. 8, pp. 7938-7947, 2014.
- [191] B. Gholipour *et al.*, "Organometallic Perovskite Metasurfaces," *Advanced Materials*, vol. 29, no. 9, pp. 1604268-n/a, 2017, Art. no. 1604268.
- [192] V. I. Levitas and M. Javanbakht, "Phase field approach to interaction of phase transformation and dislocation evolution," *Applied Physics Letters*, vol. 102, no. 25, p. 251904, 2013.
- [193] V. I. Levitas, Y. Ma, J. Hashemi, M. Holtz, and N. Guven, "Strain-induced disorder, phase transformations, and transformation-induced plasticity in hexagonal boron nitride under

- compression and shear in a rotational diamond anvil cell: In situ x-ray diffraction study and modeling," *The Journal of chemical physics*, vol. 125, no. 4, p. 044507, 2006.
- [194] A. Liu, H. Rong, R. Jones, O. Cohen, D. Hak, and M. Paniccia, "Optical amplification and lasing by stimulated Raman scattering in silicon waveguides," *Journal of Lightwave Technology*, vol. 24, no. 3, pp. 1440-1455, 2006.
 - [195] S. Reich, A. Ferrari, R. Arenal, A. Loiseau, I. Bello, and J. Robertson, "Resonant Raman scattering in cubic and hexagonal boron nitride," *Physical Review B*, vol. 71, no. 20, p. 205201, 2005.
 - [196] S. Reich, A. C. Ferrari, R. Arenal, A. Loiseau, I. Bello, and J. Robertson, "Resonant Raman scattering in cubic and hexagonal boron nitride," *Physical Review B*, vol. 71, no. 20, p. 205201, 05/04/ 2005.
 - [197] T. Werninghaus, J. Hahn, F. Richter, and D. R. T. Zahn, "Raman spectroscopy investigation of size effects in cubic boron nitride," *Applied Physics Letters*, vol. 70, no. 8, pp. 958-960, 1997/02/24 1997.
 - [198] R. Erasmus and J. Comins, "Photoluminescence spectroscopy of electron - irradiation induced defects in cubic boron nitride (cBN)," *physica status solidi (c)*, vol. 1, no. 9, pp. 2269-2273, 2004.
 - [199] J. A. Schuller *et al.*, "Orientation of luminescent excitons in layered nanomaterials," *Nature nanotechnology*, vol. 8, no. 4, pp. 271-276, 2013.
 - [200] Z. Shotan *et al.*, "Photoinduced Modification of Single-Photon Emitters in Hexagonal Boron Nitride," *ACS Photonics*, 2016.
 - [201] O. Neitzke, A. Morfa, J. Wolters, A. W. Schell, G. n. Kewes, and O. Benson, "Investigation of line width narrowing and spectral jumps of single stable defect centers in ZnO at cryogenic temperature," *Nano letters*, vol. 15, no. 5, pp. 3024-3029, 2015.
 - [202] L. Fleury, J.-M. Segura, G. Zumofen, B. Hecht, and U. Wild, "Nonclassical photon statistics in single-molecule fluorescence at room temperature," *Physical review letters*, vol. 84, no. 6, p. 1148, 2000.
 - [203] L. J. Martínez *et al.*, "Efficient single photon emission from a high-purity hexagonal boron nitride crystal," *Physical Review B*, vol. 94, no. 12, p. 121405, 09/22/ 2016.
 - [204] G. Grosso *et al.*, "Tunable and high-purity room temperature single-photon emission from atomic defects in hexagonal boron nitride," *Nature Communications*, vol. 8, no. 1, p. 705, 2017/09/26 2017.
 - [205] N. Kongsuwan *et al.*, "Suppressed quenching and strong-coupling of purcell-enhanced single-molecule emission in plasmonic nanocavities," *Acs Photonics*, vol. 5, no. 1, pp. 186-191, 2018.
 - [206] R. m. Faggiani, J. Yang, and P. Lalanne, "Quenching, plasmonic, and radiative decays in nanogap emitting devices," *ACS photonics*, vol. 2, no. 12, pp. 1739-1744, 2015.
 - [207] J. Riedrich-Möller *et al.*, "Nanoimplantation and Purcell enhancement of single nitrogen-vacancy centers in photonic crystal cavities in diamond," *Applied Physics Letters*, vol. 106, no. 22, p. 221103, 2015.
 - [208] A. F. Koenderink, "Single-photon nanoantennas," *ACS photonics*, vol. 4, no. 4, pp. 710-722, 2017.
 - [209] A. Sipahigil *et al.*, "An integrated diamond nanophotonics platform for quantum-optical networks," *Science*, vol. 354, no. 6314, pp. 847-850, 2016.

- [210] R. Chikkaraddy *et al.*, "How Ultranarrow Gap Symmetries Control Plasmonic Nanocavity Modes: From Cubes to Spheres in the Nanoparticle-on-Mirror," *ACS Photonics*, vol. 4, no. 3, pp. 469-475, 2017/03/15 2017.
- [211] P. Yao, V. Manga Rao, and S. Hughes, "On-chip single photon sources using planar photonic crystals and single quantum dots," *Laser & Photonics Reviews*, vol. 4, no. 4, pp. 499-516, 2010.
- [212] A. Requicha *et al.*, "Manipulation of nanoscale components with the AFM: principles and applications," in *Proceedings of the 2001 1st IEEE Conference on Nanotechnology. IEEE-NANO 2001 (Cat. No. 01EX516)*, 2001, pp. 81-86: IEEE.
- [213] M. H. Korayem and M. Zakeri, "Sensitivity analysis of nanoparticles pushing critical conditions in 2-D controlled nanomanipulation based on AFM," *The International Journal of Advanced Manufacturing Technology*, vol. 41, no. 7, pp. 714-726, 2009/04/01 2009.
- [214] K. Santhosh, O. Bitton, L. Chuntonov, and G. Haran, "Vacuum Rabi splitting in a plasmonic cavity at the single quantum emitter limit," *Nature communications*, vol. 7, p. ncomms11823, 2016.
- [215] R. Liu *et al.*, "Strong light-matter interactions in single open plasmonic nanocavities at the quantum optics limit," *Physical review letters*, vol. 118, no. 23, p. 237401, 2017.
- [216] J. J. Baumberg, J. Aizpurua, M. H. Mikkelsen, and D. R. Smith, "Extreme nanophotonics from ultrathin metallic gaps," *Nature materials*, p. 1, 2019.
- [217] T. B. Hoang, G. M. Akselrod, C. Argyropoulos, J. Huang, D. R. Smith, and M. H. Mikkelsen, "Ultrafast spontaneous emission source using plasmonic nanoantennas," *Nature communications*, vol. 6, p. 7788, 2015.
- [218] J. Huang, G. M. Akselrod, T. Ming, J. Kong, and M. H. Mikkelsen, "Tailored emission spectrum of 2D semiconductors using plasmonic nanocavities," *ACS Photonics*, vol. 5, no. 2, pp. 552-558, 2017.